*January*, 1930

# RUBBER CHEMISTRY AND TECHNOLOGY

*Published under the Auspices of the*
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

VOLUME III NUMBER 1

605 v. 3

# RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor.....C. C. Davis
Associate Editor.....H. L. Fisher
Secretary-Treasurer.....H. E. Simmons

Vol. III January, 1930 No. 1

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## RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

# Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

## The Rubber Division of the American Chemical Society

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## Local Group Activities

### Contribution from the New York Group

The editors of RUBBER CHEMISTRY AND TECHNOLOGY take this occasion to acknowledge the thoughtfulness and generosity of the New York Group in its support of THIS JOURNAL. At its meeting of December 16, 1929, it was voted to contribute from its funds two hundred and fifty dollars toward the growth, success and prosperity of RUBBER CHEMISTRY AND TECHNOLOGY.

### Los Angeles Group

*Sept. 20, 1929.* Address by C. R. Johnson on "Carbon Blacks."

### Akron Group

*Oct. 14, 1929.* Addresses by Clarence Moore on "Rims and Their Relation to Tires," by V. L. Smithers on "Present Tendencies in Tire Design and Construction," and by J. C. Sproull on "Indoor and Outdoor Testing of Tires." E. A. Hauser, of Frankfurt, Germany, addressed the audience, extending a cordial invitation to attend the meeting of the Society of German Rubber Chemists at Frankfurt a/M. in June, 1930.

### Chicago Group

*Oct. 25, 1929.* This was the first meeting of this newly formed group. There were addresses by R. F. Kinsley on "Factory Problems of Today," by H. B. Underwood on "Factory Problems in Tire Manufacturing," and a general address by William Welch.

# Report of the Treasurer of the Rubber Division

| | | |
|---|---|---|
| Balance in Bank at the Atlantic City Meeting | $332.42 | |
| Deposits (dues) | 138.00 | $470.42 |
| Disbursements: | | |
| Expenses of the Secretary to the Atlantic City Meeting. | $65.30 | |
| Office Supplies | 14.09 | |
| Mack Printing Co | 84.75 | |
| Express for Journals | 2.11 | 166.25 |
| Balance in Bank, December 1, 1929 | | $304.17 |

H. E. SIMMONS, *Secretary-Treasurer*

# New Books and Other Publications

**"Summary of Current Literature."** Vol. VII, No. 5. Research Association of British Rubber Manufacturers, Information Bureau, 105 Lansdowne Road, Croydon, England. Paper, 64 pages, $7^1/_4$ by $9^3/_4$ inches.

This is a typical number of the summary of current literature issued each month to provide the members of The Research Association of British Rubber Manufacturers and subscribers with the recorded developments in connection with materials, products, and processes. This publication covers every phase of the rubber industry from the production of the raw material to its many and varied applications in service. It includes reference to, or an abstract from every article of importance dealing with rubber which has appeared in the technical and scientific press during the preceding month.

The summary is accepted by progressive manufacturers in Great Britain as practically indispensable as a means of keeping in touch with the latest scientific and technical developments and as a valuable time-saver for their factory and technical executives in consulting the ever-increasing volume of matter relating to rubber and allied subjects. [From *India Rubber World.*]

**"Les Progrès de la Technologie du Caoutchouc."** Dr. F. Kirchhof. Translated from the German into French by W. Demarche and A. Andrien. Published by Librairie Polytechnique Ch. Beranger, Paris and Liege. 1929. Cloth, $6^3/_8$ by $9^3/_4$ inches, 272 pages, graphs, diagrams, tables, illustrations, indices.

The French translators of this work by Dr. Kirchhof have carefully followed the original German. Here and there, however, with the author's consent they have made certain changes. This book was destined for rubber technologists, particularly for men with scientific and technical backgrounds but lacking the time and means of following up German and foreign rubber articles and patents.

The present volume is divided into twelve chapters. The first three deal with the production of rubber, latex, and modern methods of preparation; the next three with the working of crude rubber, fillers, and mixings, solvents and solutions. Chapters VII and VIII treat of vulcanization and accelerators; the following two are devoted to rubber reclaiming, synthetic rubber, hydro-rubber, cyclo-rubber and other high polymers. The latest uses and possible future uses of rubber, such as tires, bands for caterpillar-tractors, and paving are discussed in Chapter XI, and the twelfth chapter is devoted to mechanical testing of rubber. An index of names of authors and firms and a general index complete the work. [From *India Rubber World.*]

**"Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry."** Vol. III, 1928. Society of Chemical House, 46 Finsbury Square, London, E. C. 2. Cloth, 741 pages, $5^1/_2$ by 8 inches. Indexed.

This yearly volume of reports summarizes the advances and discoveries made in various branches of technology. The chapter on rubber occupies 21 pages by D. W. Twiss, who cites as the feature of greatest popular interest in the rubber industry during 1928, the sudden decision of the British Government to end the Stevenson Scheme for restriction of the output of rubber from British plantations.

The following topics are discussed concisely with copious references to their scientific and technical developments: rubber planting; latex; raw rubber; vulcanization; compounding ingredients; rubber treatment and applications; and testing.

The reports and references contained in this publication are invaluable for

chemists as they are summarized by specialists in each field of chemical technology. [From *India Rubber World.*]

**Annual Report (1928) Including Initial Period.** Published by the Rubber Research Institute of Malaya. Paper, $6^1/_8$ by $9^3/_4$ inches, 128 pages.

The Rubber Research Institute was established in September, 1926, with Dr. Bryce as director. About a year ago severe criticism was directed against him and his work, culminating in the termination of his contract with the Institute. His report of the Institute's activities furnishes interesting material.

During the period November, 1926—December, 1928, 304 visits were paid to 250 estates, experiments were conducted on 42 estates, 49 lectures were delivered before various planting associations and other organizations by the director and his staff, and no fewer than 2909 letters from planters on the most varying problems of rubber planting were handled. The different departments investigated a number of special problems as budding, and the physiology of latex production, manufacturing crepe and sheet, and concentration of latex, combating pests and diseases, etc. [From *India Rubber World.*]

**"Annual Report and Year Book, 1928-1929,"** has been issued by the Planters' Association of Malaya, Inc., Kuala Lumpur, Federated Malay States. This book contains the report of the association for the year ended March 31, 1929. It gives also information on Indian, Chinese, and Netherlands Indian labor, health boards, and game laws, as well as on cocoanuts and copra. To rubber are devoted two chapters, one on rubber itself and the other on diseases and pests of *Hevea*, cover plants, manuring, budgrafting, and seed selections, etc. The book concludes with miscellaneous notes and appendices. It provides a wealth of data regarding Malaya, supplemented by statistics and tables. $5^7/_8$ by $8^3/_8$ inches, cardboard covers, 198 pages. [From *India Rubber World.*]

**Kautschuk, Tier- und Pflanzenfette, Wachse.** Victor Grafe. Paper cover only. C. S. Poeschell, Stuttgart, 1929.

This work is a part of the authoritative treatise on organic merchandise, including the mechanical technology and testing. It comprises the following three sections: (1) Rubber, gutta-percha and balata, by V. Grafe of the University of Vienna and the new Commercial Academy of that city. The author describes in detail raw rubber, its preparation and its properties, and follows with a description of the important branches of rubber technology. (2) Chemistry of fats and waxes. Animal fats. Industries using fats. Waxes. By A. Jolles of the High School of Commerce at Vienna. (3) Vegetable fats and waxes. Industrial applications. By K. H. Bauer. In this section there is information in detail on the preparation of fats, their applications (soaps, candles, varnish, oil colors, etc.), the technical analysis of fats, varnishes and colors, artificial edible fats, etc. A short appendix is devoted to cork. This work is of interest to a great number of industries, including that of rubber, linoleum, cosmetics, margarines, soap, and cork. The work also contains valuable information for economists and commercial men in various fields, for the subjects treated in this volume are important in our daily economic life and will have a greater and greater influence, for which it is sufficient to call attention to the tire and margarine industries. This book is published in perfect style, and is illustrated with 85 pictures. [From *Caoutchouc & Gutta-percha.*]

**Agricultural Zoology of the Malay Archipelago.** The Animals Injurious and Beneficial to Agriculture, Horticulture, and Forestry in the Malay Peninsula, the Dutch East Indies, and the Philippines. By K. W. Dammerman. Published by J. H. de Bussy, Ltd., Amsterdam, Holland. 1929. Price, 40s.

While in the main an English edition of the author's previous work on the

Dutch East Indies, published ten years ago, this volume has been extended in scope and includes descriptions of the animal pests, soil fauna, and plant parasites of all the territories mentioned in the title. The pests and parasites harmful to the *Hevea brasiliensis* and *Ficus elastica* are described in detail with life-size color plates of the insects. [From *The Rubber Age* of New York.]

**The Natural Coagulation of Latex.** A. S. Corbet. Published by the Rubber Research Institute of Malaya, Kuala Lumpur, Federated Malay States, 1929. Twenty-four pages.

This bulletin is the first of a series which the Rubber Research Institute of Malaya intends to publish from time to time when scientific or technical researches on some particular subject have been carried to a point suitable for publication. The present bulletin contains the results of researches which confirm and carry further previous researches of the Department of Agriculture (Straits Settlements and Federated Malay States), of the Rubber Research Scheme of Ceylon, of the Experimental Station of Rubber in Java and Indo-China and of the former Department of Research of the International Society of Plantations and Finance in Malay. The bacteriological study of the latex of *Hevea brasiliensis* has shown the predominance of one organism. The characteristics and the biochemical reactions of this organism have been studied in detail, and since this organism seems not to have been named previously it is proposed to call it by the name of Bacillus pandora. The B. pandora is capable of decomposing certain substances in latex, with formation of acid, as a result of which the separation of rubber is induced. Following this phenomenon, it attacks the proteins with formation of ammonia. This organism is then the cause of acid serum and of the superficial alkaline stratum observed during the natural coagulation of latex. The author discusses the reason for the use of ammonia and of sodium sulfite for preserving latex. [From *Caoutchouc & Gutta-percha.*]

**Rubber Producing Companies—1929.** Published by the Mincing Lane Tea & Rubber Share Brokers' Association, Ltd., 14 Mincing Lane, London, Eng.

As the first edition of this standard guide to be issued after the termination of the Stevenson Act restrictions, this volume is of special interest. The work follows the lines of previous editions, giving exhaustive data relating to over 600 companies. A list of directors and secretaries of rubber plantation companies is also given. [From *The Rubber Age* of New York.]

**South American Markets for Rubber Sundries and Specialties.** Compiled by the Rubber Division, Department of Commerce. Published by the Government Printing Office, Washington, D. C. 1929. Price, $0.10.

South American countries are each year increasing their purchases of United States rubber sundries and specialties. Last year American shipments of these products to South American markets reached a value of nearly $700,000, representing about 12 per cent of our total exports of these commodities. The high lights in connection with marketing soft rubber products in the South American republics are outlined in this bulletin, particularly the competitive conditions, the demand, and methods of doing business. [From *The Rubber Age* of New York.]

**"Foreign Markets for Rubber Boots and Shoes and Rubber Heels and Soles, Section III, Latin American Countries,"** is a 44-page paper booklet issued under the supervision of E. G. Holt, Chief, Rubber Division, Department of Commerce, Washington, D. C. The preface by Mr. Holt gives a brief résumé of the situation. Then, in tabular form, with separate pages devoted to each of the twenty Latin American countries considered, are given statistics on foreign imports and exports as well as their value of rubber boots and shoes and rubber heels and soles. [From *India Rubber World.*]

**"The Crepe Rubber Sole (Plantation Finished) Handbook for Repairers."** This 20-page illustrated booklet is issued by The Rubber Growers' Association, Inc., 2 Idol Lane, Eastcheap, London, E. C. 3, England. It contains full and explicit directions on the procedure for repairing leather shoes with crepe soles and heels. Every step is pictured as well as described, and the instructions cannot fail to be of service to shoe repair men wherever crepe soling is available. [From *India Rubber World.*]

**Some Properties of Sponge Rubber.** Prepared by the Bureau of Standards, Department of Commerce. Published by the Government Printing Office, Washington, D. C. 1929. 12 pp. Price, $0.05.

General information on soft sponge rubber as commercially manufactured and certain data on the physical properties of 13 different samples of sheet material are furnished by this paper. The properties investigated included weight per unit volume, hardness, porosity, tensile strength, and elongation, permanent "set," buoyancy in water, hysteresis under slow compression, hysteresis under impact, and thermal conductivity. [From *The Rubber Age* of New York.]

**Conveyors.** Published by the National Safety Council, 108 East Ohio Street, Chicago, Ill. 1929. 8 pp.

Belt conveyors and eleven other types of conveyors are considered in this revised edition of Safe Practices Pamphlet No. 35. General and specific suggestions for the use of each type, compiled from actual experience in accident prevention, make up the text of the paper. [From *The Rubber Age* of New York.]

**Combination Inner Tube Patch Material.** Laboratory Report No. 131-A, E. I. DuPont de Nemours & Company, Dyestuffs Department, Rubber Laboratory, Wilmington, Del.

The report covers the results of three years study in producing a face stock for repair materials which will remain tacky under all conditions of vulcanization and storage. Inner tube repair material made by spreading the unvulcanized face material, containing no vulcanizing agent, on the vulcanized back is expensive and at times unsatisfactory because of the poor adhesion between the two portions. The most serious objection to the more modern method of calendering together the backing containing sulfur and accelerators and the face stock without vulcanizing agents is that accelerators and sulfur have a tendency to migrate to the face during the cure. Recommendations are given in this report for overcoming these objections by the proper use of raw materials and compounding ingredients, and suggestions are also made as to manufacturing methods and curing. [From *The Rubber Age* of New York.]

**Cotton from Plant to Product.** Published by the Pepperell Manufacturing Company, 160 State Street, Boston, Mass. 1929. 68 pp.

In response to numerous requests from students, teachers, sales representatives, and others for a book on cotton and its manufacture stripped of technical terms and treated in popular style, this attractive little volume has been prepared by a leading manufacturer. It is copiously illustrated and tells in simple language how cotton grows and what happens to it after it has been picked in the fields. [From *The Rubber Age* of New York.]

**"Cotton in the Rubber Tire and Tube Industry"** by Herbert A. Ehrman, Textile Division, is Bulletin No. 6 in the New Uses for Cotton Series, which deal with the possibility of increase in the use of cotton products, issued by the Department of Commerce, Bureau of Foreign and Domestic Commerce, Washington, D. C. This twelve-page paper booklet treats of the various uses cotton is put to in the tire industry, ranging from tire casings to the cotton gloves the worker wears for

protection. The data are supplemented by tables and a diagram. [From *India Rubber World.*]

**"Zinc Oxide as a Rubber Pigment."** Issued by The New Jersey Zinc Co., 160 Front St., New York, N. Y. Paper, 32 pages, 6 by 9 inches.

This report from the research laboratory of The New Jersey Zinc Co. is contributed as a part of its work in the interests of the rubber industry. In it are discussed all the essential features of zinc oxide as a rubber compounding ingredient. These include the general properties it imparts to rubber: namely, wettability, good heat conductivity and low heat generation, high heat capacity and combined effect of low heat generation and good heat dispersion.

The properties of zinc oxide in rubber, which depend upon the kind or quality of the zinc oxide used, are reviewed under the headings: 1, activation; 2, rate of cure; 3, reënforcement; 4, aging; 5, factory working qualities; and 6, color.

The company's products and processes are briefly mentioned. The pamphlet closes with a very full bibliography of technical papers and patents relating to zinc oxide. [From *India Rubber World.*]

**Two Years' Experience with Certified Carbon Black.** By C. R. Johnson. Published by Godfrey L. Cabot, Inc., Boston, Mass. 1929. 28 pp. For free distribution.

Control of the quality of carbon black has been a difficult problem for technical men for many years. Despite the well-known fact that there were marked variations in the reinforcing properties of various carbon blacks, these could not be detected by any specifications except an actual test in rubber. The volatile matter test, which has since been devised, is described in this attractive paper and the means by which it permits actual control of variability are outlined in detail. An appendix lists the results of 27 physical tests on good, medium, and poor quality carbon blacks with various accelerators, proving that quality variation in the blacks does effect the rubber test. [From *The Rubber Age* of New York.]

**"A.S.T.M. Tentative Standards 1929."** American Society for Testing Materials, 1318 Spruce St., Philadelphia, Pa. Paper or cloth, 901 pages, 6 by 9 inches. Indexed, illustrated.

This volume just off the press contains the following Tentative Standards relating to rubber—twenty-five standards for rubber products, insulating materials, and textile materials. [From *India Rubber World.*]

**"1929 Supplement to Book of A.S.T.M. Standards."** American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Paper, 293 pages, 6 by 9 inches.

This pamphlet is the 1929 supplement to the 1927 edition of the triennial publication, "Book of A.S.T.M. Standards." The supplement contains nineteen revised and thirty-two newly adopted standards. The pamphlet is so arranged that one can separate that portion relating to metals from that relating to non-metals if desired. Of special interest to rubber engineers of tests are the following: Specifications and Tolerances and Test Methods for Certain Light and Medium Cotton Fabrics; Specifications and Tolerances for 23/5/3 Carded American Tire Cord; Tolerances and Test Methods for Asbestos Yarns. [From *India Rubber World.*]

**"Chemical Engineering Catalog."** Fourteenth Edition, 1929. Published by The Chemical Catalog Co., Inc., New York, N. Y. Cloth, illustrated, 1205 pages, 9 by 12 inches.

This well-known standard reference work annually revised and enlarged is invaluable as a compendium of technical data for chemists, chemical engineers, and manufacturers. It contains an alphabetical index and trade name index covering

the four sections of the volume which are as follows: Classified Index of Equipment and Supplies; Equipment and Supplies Section; Classified Index of Chemicals and Raw Materials Section; Technical and Scientific Book Section. Each successive annual edition registers improvement over the one preceding and the present edition is no exception. The catalog is distributed in the United States and Canada under two alternative plans—sent free of charge to holders of certain classified industrial positions; others pay a designated charge to cover mail and express. [From *India Rubber World.*]

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# A Survey of Recent Literature on the Chemistry of Rubber

## Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the October 10 and 20, and November 10 and 20, 1929, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

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**Jelutong.** C. D. V. GEORGI. *Malayan Agr. J.* **17**, 101–17(1929).—Since Fe compds. have been shown to induce the oxidation of jelutong (cf. *C. A.* **23**, 546) and since jelutong can, during its prepn., be easily contaminated with Fe, expts. were carried out to det. at what stage Fe has the greatest influence. The expts. with Cu and Mn compds. were repeated, the reputed tendency of Kedah jelutong to oxidize was investigated further, and the behavior of creped jelutong in storage was detd. In the new expts. various proportions of aq. $(NH_4)_2Fe_2(SO_4)_4$ were added to the latex, the latter was then coagulated with $H_2SO_4$, let stand 4 days, squeezed and left without further treatment or refined with boiling water. The results show that very small proportions of sol. Fe salts induce rapid oxidation, without the growth of mold, even 1 part of sol. Fe in 20,000 parts of latex causing complete oxidation after 3 months, in which case only 60% of the Fe originally added was found in the oxidized product. Jelutong refined with boiling water did not oxidize nearly so rapidly (because of the smaller Fe content of the corresponding samples), though here too oxidation was well advanced after 4 months. Treatment with boiling water also increased the toughness. The same general results were obtained with $FeCl_3$, with AcOH as coagulant. When jelutong latex contg. Fe salts was coagulated by boiling, the product was also susceptible to oxidation in much the same way, even after refining with boiling water. Expts. with rusty coagulating app. showed that wherever spots of rust existed in the jelutong, oxidation ensued. When $Fe_2O_3$ was mixed with latex before coagulation with $H_2SO_4$ or coagulation by boiling, black mold developed, but there was no oxidation. There was no oxidation of jelutong prepd. by soaking the coagulum in water contg. $Fe(OH)_3$ (1–40 parts of Fe per 100,000 parts of water) and refining with boiling water after 4 days. Contact of the surface of refined jelutong with aq. $FeCl_3$ $(NH_4)_2Fe(SO_4)_4$ and $Fe(OH)_3$ and rusty nails caused little or no oxidation. Addn. of $CuSO_4$ (1 part of Cu per 2500–10,000 parts of latex) and coagulation with AcOH yielded products, which, whether or not they were refined with boiling water, showed no signs of oxidation. Similar treatment, except for coagulation with boiling AcOH, yielded products which with the higher proportions of $CuSO_4$ were completely oxidized after 4 months. Similarly, $MnCl_2$ and $MnSO_4$ (1 part of Mn per 1000–4000 parts of latex) yielded products which did not oxidize, and which showed no abnormal growth of mold. The higher proportions of Mn tended to retard coagulation. In general, the results agree with those of the earlier expts. (*loc. cit.*). Fe is the most dangerous metal of those tested, but it is objectionable only if in sol. form in the latex. An investigation of Kedah jelutong showed no evidence in support of the view that this jelutong is particularly prone to oxidation. Expts. also show that creped jelutong has no greater tendency to oxidize than the corresponding uncreped product. C. C. D.

**Microscopic investigations on the occurrence of resins in Hevea latex.** A. FREY-WYSSLING. *Arch. Rubbercultuur* **13**, 371–91(1929). (In English 392–412.)—A systematic study of latexes of different origins led to the discovery that there are present among the rubber particles a hitherto unsuspected kind of globule which has the same appearance as the rubber particles but which consists of *resin*. These colorless globules of resin carry the *yellow pigment* of latex, and it was because of this that they were first detected in latex from trees which yielded a yellow latex. They occur not only in the latex of *Hevea brasiliensis*, but also in that of *H. guianensis*, *H. collina* and *H. spruceana*, in the latter in relatively great quantities. Their dimensions are about the same as those of the rubber particles. They refract light somewhat more; they are viscous

and of a butter-like consistency; and they cohere far better than rubber particles. Unlike rubber particles they can be stained by fat coloring dyes, and unlike rubber particles they are sol. in EtOH, AcMe and AcOH. They contain several components, including various esters of fatty acids and at times the yellow pigment. They are unaffected by $NH_3$, $Na_2CO_3$, $Na_2SO_3$, $NaHSO_3$ and $Na_2S_2O_3$, but are liquefied by 40% aq. HCHO. No peroxidase is present. They reduce 1% osmic acid and $AgNO_3$, and are oxidized by $HNO_3$ and by $KMnO_4$. Though the yellow pigment is absorbed in the resin there is no quant. relation between the resin content and the pigment content of the latex. If pigment formation is abundant, yellow latex results, whereas with only a slight tendency to form pigment the latex is white. Colorless resin globules also occur in branches and in very young latex next to the cambium, and in general, the formation of resin globules in latex is just as characteristic of the rubber tree as the formation of rubber particles. C. C. DAVIS

**Latices of Euphorbia tirucalli, E. candelabro and E. abyssinica.** E. DE'CONNO, S. CAPALBI AND L. FRUITIER. *Ann. chim. applicata* **18,** 540–9(1929).—All plants of the *Euphorbia* family contain some latex. The varieties found in Tirucalli, Candelabro and Abyssinia have been investigated. They contain, resp., $H_2O$ 46.8, 30.05, 49.6%; gums 7.25, 8.3, 8.44%; insol. residue 10.1, 9.8, 2.02%. All also contain traces of fatty substances. A. W. CONTIERI

**The swelling of rubber.** P. STAMBERGER AND C. M. BLOW. *Nature* **124,** 13 (1929).—Expts. on the diminution of the vapor pressure of solvents in rubber jellies and on swelling pressures show that the vapor pressure of jellies is a const. at a given concn. of rubber, regardless of the kind of rubber and the extent to which it has been masticated (cf. S., *C. A.* **22,** 2078). However, after mastication swelling is unlimited and up to 30% concn. a viscous liquid is obtained, which shows that the solvent is not bound by surface adsorption. The relative vapor-pressure-concn. curve differs from that calcd. by Raoult's laws, the curve bending sharply at 20–30% concn. toward the vapor-pressure axis, which suggests that the phenomenon is more complicated than ordinary soln. Though no difference was found between the vapor pressure of "liquid" jelly from masticated rubber and solid jelly from untreated rubber, the swelling pressures were far different, showing that the swelling of a structureless rubber differs greatly from that of a rubber with a well-defined structure, though both show the same diminution of vapor pressure. It is impossible, therefore, to calc. the swelling pressure from the vapor-pressure diminution on a thermodynamical basis. The expts. show that the forces which cause imbibition of solvent by jelly are not uniform, a "structure factor" taking a part when the solvent is in liquid form. C. C. DAVIS

**The influence of the amount of the surplus liquid on the swelling maximum of rubber jellies.** C. M. BLOW AND P. STAMBERGER. *Rec. trav. chim.* **48,** 681–94(1929); cf. *C. A.* **22,** 4314; **23,** 3144.—Rubber jellies in PhMe, petroleum ether or $C_6H_6$ show an increasing swelling max. with an increase in the initial vol. of liquid present, up to a point beyond which a greater vol. of liquid causes no greater swelling max. The variations are due to the rubber diffusing into the solvent during the process of swelling to different extents when different proportions of liquid are present. The effect of a higher temp. during swelling is to increase the swelling max. The proportion of rubber in a gel was detd. by drying the gel and weighing. It was found that the concn. of rubber in the unabsorbed liquid was greater, the less the proportion of pure liquid present initially. The jelly swells less, the higher the concn. of rubber in the final liquid. Nearly the same final state was observed when rubber was swollen in solvents initially contg. varying proportions of rubber, and when jellies swollen to a max. were transferred to solns. contg. varying proportions of rubber. Variations in the swelling max., due to change in the concn. of the rubber in the unabsorbed liquid, can be explained qual. on the assumption of an osmotic phenomenon. CORNELIA T. SNELL

**Cold vulcanization [of rubber] (Parkes' process).** P. BOURGOIS. *Bull. fédération ind. chim. Belg.* **8,** 3–8(1929).—The method of vulcanization of rubber by immersion in a soln. of $S_2Cl_2$ is reviewed, with especial reference to certain practical details and difficulties. The vulcanizing effect is attributed to nascent S formed from the $S_2Cl_2$ by the action of natural moisture in the rubber. B. C. A.

**Topochemical reactions with racked rubber.** F. KIRCHHOF. *Kautschuk* **5,** 9–13 (1929).—When immersed in $H_2SO_4$ (d. 1.8) for 4 months, thin strips of smoked sheet rubber which had been racked to 600% darkened and lost their power of contraction in warm water. A fibrous structure was, however, still evident both from visual examn. and by the production of a distinct point diagram with x-rays. Treatment of similarly racked rubber with Br water also yielded a product with a superficially fibrous character, but x-rays revealed no sign of any structure, even the amorphous ring being absent. Apparently bromination causes a complete structural disturbance both in the

amorphous component and in the crystallites, whereas with $H_2SO_4$ the action appears to be confined chiefly to the amorphous phase. C. C. DAVIS

**The problem of vulcanization without sulfur.** LEO ECK. *Gummi-Ztg.* **43**, 2481–2 (1929).—A discussion of present knowledge, with particular reference to the work of Ostromislenskii (cf. following abstr.). For vulcanization without S to be successful economically: (1) the new process must be no longer nor more difficult than that with S; (2) the phys. properties of the vulcanizates, including their aging, must be at least as good as those of the corresponding vulcanizates with S; (3) the vulcanizing agent must be innocuous; and (4) if the vulcanizing agent gives no better results than does S, it must be cheaper. The fulfilment of these conditions by 1,3,5-$C_6H_3(NO_2)_3$ is open to question. C. C. DAVIS

**Vulcanization without the use of sulfur.** IVAN OSTROMISLENSKII. *India Rubber World* **80**, No. 3, 55–61(1929).—Because of contradictory results obtained by other investigators on the vulcanization of rubber with 1,3,5-$C_6H_3(NO_2)_3$, and to furnish quant. data on the methods and results obtained by O. (which were not published in complete form in the original papers of O.), the earlier expts. are reviewed and discussed and quant. data not heretofore published are given. The commonest error in using 1,3,5-$C_6H_3(NO_2)_3$ is to use too much. Over 3% should never be used, and 2% is better (based on the wt of rubber). All mixts. should contain an agent to protect the vulcanizates against aging, *e. g.*, relatively large proportions of oxides (PbO, ZnO, etc.) or 0.3–1.0% of aromatic amine. Rubber mixts. vulcanized with 1,3,5-$C_6H_3(NO_2)_3$ often have phys. properties superior to the corresponding mixts. with S. The aging in particular is better with the 1,3,5-$C_6H_3(NO_2)_3$ vulcanizates. A sample 13 yrs. old has shown little or no change in phys. properties. With suitable accessory ingredients, rubber mixts. can be vulcanized at 50–100° with 1,3,5-$C_6H_3(NO_2)_3$. With the latter, overcuring is minimized, *e. g.*, a mixt. of rubber 100, 1,3,5-$C_6H_3(NO_2)_3$ 2, $PhNH_2$ 1, ZnO 150, has almost the same phys. properties whether cured for 20 min. or for 2 hrs. at 141°. Carborundum, Si and certain other uncommon ingredients accelerate the action of 1,3,5-$C_6H_3(NO_2)_3$ and impart peculiar phys. properties to the vulcanizates. Deterioration through contact with Cu or by acids is slower in vulcanizates cured with 1,3,5-$C_6H_3(NO_2)_3$ than in those cured with S. Metallic oxides, sulfides, selenides and tellurides, C black, lamp black, amorphous C, graphite, Si, SiC, red P, Al, talc, ultramarine and other substances accelerate the action of 1,3,5-$C_6H_3(NO_2)_3$, whereas amorphous B is not an accelerator. C black, whether it is or is not satd. with air, accelerates in the same way, so it does not act as an O carrier. With a chem. and a phys. accelerator together, *e. g.*, with a metallic oxide and C black, the effect is additive. The character of the ZnO governs to a great extent its accelerating power. Thus a mixt. of rubber 100, 1,3,5-$C_6H_3(NO_2)_3$ 2, ZnO 150, cures in 20–25 min. at 141° with "Kadox" ZnO, whereas with ordinary ZnO the cure is 160 min. at 141°. C black is also an excellent accelerator with 1,3-$C_6H_4(NO_2)_2$. With PbO and C black, 0.25–0.5% of 1,3,5-$C_6H_3(NO_2)_3$ (based on the wt. of rubber) is the min. required for satisfactory vulcanization. The presence of S (0.3–8.0%) or of ordinary accelerators does not influence the rate of vulcanization with 1,3,5-$C_6H_3(NO_2)_3$. With 2–8% S (there is a discrepancy between these values and those above—ABSTRACTOR) or with a large proportion of aliphatic or aromatic amine, the rate of vulcanization with $NO_2$ compds. is retarded and the phys. properties of the vulcanizates are impaired. Aromatic amines, S, metallic sulfides and above all $Sb_2S_5$, certain S dyes and tannic acid protect 1,3,5-$C_6H_3(NO_2)_3$-vulcanizates from oxidation and other changes occurring on storage in the open air. The proportion of these protective substances should be limited to 0.3–1.0%. A few representative factory rubber mixts. cured with 1,3,5-$C_6H_3(NO_2)_3$ had superior phys. properties for the particular uses to the corresponding mixts. cured with S. C. C. DAVIS

**Chemical analysis of gutta-percha, balata and allied gums.** S. MINATOYA, K. ISHIGURO AND K. MARUYAMA. *Res. Electrotechn. Lab., Japan* No. **232**, 14 pp.(1928).—Chem. analysis is of great importance in research on gutta-percha, balata and allied gums for submarine cable insulation. The authors collected 26 kinds of gutta-percha, 8 kinds of balata and 3 varieties of allied gums with trade names, and analyzed them for moisture, ash, dust, resin and gutta hydrocarbon. The resin, which has the most influence on the elec. and mech. properties, was subdivided into the so-called "fluavile," "spherical albane" and "needle albane." W. OGAWA

**The gutta-percha-like substance obtained from Tu-chung.** S. MINATOYA AND K. ISHIGURO. *Res. Electrotechn. Lab., Japan* No. **260**, 16 pp.(1929).—The characteristics of the gutta-percha-like substance derived from the bark of Tu-chung were investigated with a view to applying it to insulating material for submarine cables. By extn. it was found that the air-dried bark contains moisture 9.88, resinous 14.65 and gutta-like hydrocarbon 6.46%. The elec. and mech. properties of this hydrocarbon are as good as those of gutta-percha. Elementary analysis and the I value showed

that this hydrocarbon is a polymer of isoprene or $(C_5H_8)n$. The authors also detd. the change of plasticity with temp., softening point, tensile strength, elongation at break, hardness, elasticity, water absorptive power, resistance to chemicals, elec. puncture voltage and power factor of the hydrocarbon. W. OGAWA

**A study of the viscosity of rubber latex.** C. M. BLOW. *Trans. Faraday Soc.* **25**, 458–62(1929).—Samples of different latexes were dild. to different degrees and their viscosities detd. as a function of concn. For diln. the serum of the same latex was used, so as not to introduce new variables arising from colloidal changes which might take place if water was added. From the viscosity values of the dild. latexes, the vols. of the dispersed phase were calcd. by the Einstein formula, taking as the viscosity of the dispersion medium that of the original serum. The shape of the concn.-relative viscosity curves is very nearly similar to that of Borrowman (cf. *Rubber Industry* **1911**, 243). There is a deviation from the equation of Einstein, but this equation is valid at low concns. In some there was a slight increase of vol., which may have been caused by the presence of an adsorbed, hydrated layer. On diln. with water, the viscosity and content of the dispersion medium changed as a result of the adsorbed layer going into soln., the viscosity of the dild. serum being lower than that of the serum obtained from latex of the same concn. The thickness of the adsorbed layer was 0.10 $\mu$ in the extreme case. The viscosity of a latex depended greatly upon the viscosity of its serum. C. C. DAVIS

**Heat effects which accompany the spontaneous increase in density of raw rubber.** H. SACHSE. *Gummi-Ztg.* **43**, 2216, 2218(1929).—The *heats of swelling* of various samples of rubber were measured in a specially designed *calorimeter*, which is described and illustrated and which employs $Ph_2O$ as the dilatometer liquid. By assuming that all samples reach practically the same final state of energy, it is possible to obtain the energy difference of the original state and the heat tone of the spontaneous process, which make the rubber more dense, from the difference between the heats of swelling. The samples included (1) crepe which had been stored 10 yrs. at room temp. and had lost its rubbery properties; (2) hot-milled crepe which had been stored several yrs. at room temp. and still showed a calender effect; (3) para rubber; (4) crepe elongated, fixed and stored several days; and (5) the foregoing samples expanded by storage at 40–50° and then at 20°. Crepe (1) required higher temps. for expansion than (2), the expansion of (2) being complete on warming to 40°. Crepe (5) was particularly interesting, for here a neg. heat effect was obtained at first, followed by a pos. effect. The following data give the sample, the heat effect (in cals.) at 0° and the heat effect at 26.55°, resp.: (1), —8.17, —6.22; (1) (expanded), —1.6, —1.62; (2), —2.16, —; (2) (expanded), —1.34, —1.51; (3), —1.93, —; (3), (expanded), +0.70, +1.70; (4), —2.83, —5.52 (fixed and stored 3 months); (5), —, —0.5 to —1.0. The highest observed value of the heat of condensation of crepe which had not been first treated mechanically was approx. 6.4 cals. per g. This represents the extreme case of condensed rubber which is no longer elastic. Milled rubber samples which had been elongated and fixed showed lower values, which correspond to their power of further condensation. To this may also be attributed the more ready expansion on increase of temp., which is complete at 40°, whereas the crepe, which had been stored for 12 yrs. and was completely condensed, expanded only at higher temps. from 60° to 80°. C. C. D.

**The crystal structure of Tjipetir gutta-percha. (Comparison with frozen rubber.)** F. KIRCHHOF. *Kautschuk* **5**, 175–83(1929); cf. *C. A.* **23**, 1525.—Purified Tjipetir gutta-percha is a particularly good product for studying the cryst. structure of the gutta-percha hydrocarbon. It was dissolved in $C_6H_6$ at 80° (16% soln.), filtered, let stand several days at 15° and decanted, which left a mass of microscopically small spherolitic dendrite crystals. Cooling the mother liquor to 10–12° deposited further microcrystals of clustered dendritic form. When the 16% $C_6H_6$ soln. was let stand 14 days at 15° and then cooled to 0°, delicate fibrous or needle crystals were deposited, followed by complete gelation. On warming any of the solns. above a certain temp. range (24–5°), a clear soln. was again obtained. The deposit of gutta-percha from $C_6H_6$ thus depends upon the temp. and the rate of cooling, as with monomol. fusions or 2-phase hydrosols, *e. g.*, Na oleate. The formation of cryst. nuclei also depends upon the concn. Various other details of the crystn. phenomena are described and illustrated by photomicrographs. The viscosity of the solns. varied in direct proportion to the temp. between 10.5° and 40.5°, but below this range flocculation upset the results. This linear relation is probably a resultant of compensation between the decrease in concn. and the increase in micellar friction. The com. pure gutta-percha melted at 62–4° and froze at 42°, the more highly purified spherolitic dendrites at 66° and 45°, resp., and the needle form at 64–5° and 41–3°, resp. The original material probably contained oxidation products. There was not only a temp. hysteresis between the m. p. and f. p. but also a time hysteresis, both of which are also true of frozen rubber (cf.

van Rossem, *C. A.* **23,** 2320). This time hysteresis was far shorter with solid gutta-percha than in $C_6H_6$, and after crystd. gutta-percha had once been fused its subsequent crystn. was more rapid, perhaps because of the presence of cryst. nuclei. The d. of crystd. gutta-percha was distinctly higher than that of fused gutta-percha or of rubber, the d. of dendritic gutta-percha, fused and partially crystd. gutta-percha, fused gutta-percha, frozen rubber and fused rubber being 0.977–0.992, 0.959–0.960, 0.938–0.939, 0.930–0.945 and 0.900–0.910, resp. The results indicate that the hydrocarbon of gutta-percha is different from that of rubber. Gutta-percha may, however, be a *trans* and rubber a *cis* form of the same hydrocarbon, so that in some cases the same derivs. are obtained. C. C. DAVIS

**New American standards for the correct formulation of rubber mixtures according to the conditions prevailing in February, 1929.** WERNER ESCH. *Gummi-Ztg.* **43,** 2536, 2586–8(1929).—A review and discussion of the most recent practice. C. C. D.

**Rubber and its fractions.** R. PUMMERER. *Kautschuk* **5,** 129–35(1929).—A review and discussion, with new points of view and new data. Detns. of the I no. and of the O no. (with perbenzoic acid) of various sol and gel fractions of alkali-purified latex, Revertex, crepe and smoked sheet showed that, in general, gel-rubber requires more $ICl_3$ and more per benzoic acid than sol-rubber (based on the % of the theoretical per double bond per $C_5H_8$ group), the values for the gel-rubbers running well over 100 and those of the sol-rubbers 100 and below. Gel-rubber is, however, probably more unsatd. than sol-rubber, for no differences in the addn. of HCl or of PhNO were found. The evolution of HCl with $ICl_3$ is fundamentally different, no HCl being detected with sol-rubber, whereas with gel-rubber 5% of the halogen consumed is evolved as HCl, indicating either substitution or cyclicization. By assuming substitution, calcns. show that sol-rubber and gel-rubber have the same no. of double bonds. Other evidence suggests a difference in the configuration (*cis* and *trans*) or in the micelles. By warming, sol-rubber becomes similar to gel-rubber, its viscosity and tenacity increasing and its chem. properties (titer) also approaching those of gel-rubber. The decrease in viscosity found by Staudinger and Bondy (cf. *C. A.* **23,** 3372) can be explained by the fact that air was not excluded and, furthermore, the rate of cooling affects the viscosity, sol-rubber in $C_6H_6$ being more viscous when cooled slowly after heating than when cooled rapidly. This latter fact indicates a micellar structure of rubber solns. The cooling effect is as great as the total heating effect if cooling is slow. The osmotic pressure is primarily an indication of the tendency of rubber to swell, and it is not a measure of the size of the mol. Cryoscopic and osmotic measurements are sometimes contradictory, and in such cases the cryoscopic method may be erroneous because of the *crystn. of complex phases of rubber and solvent.* In expts. on this subject, crystals of $C_6H_6$ contg. 0.74–0.85% rubber were obtained. This tendency to form rubber-$C_6H_6$ crystals may be utilized for the further purification of rubber. A general discussion follows the paper. C. C. DAVIS

**The optical anisotropy of stretched rubber.** H. ZOCHER WITH H. J. V. FISCHER. *Kautschuk* **5,** 173–5(1929).—A Berek calcite compensator was used for measuring the double refraction of stretched rubber, the complete app. including a means for the uniform bilaterally symmetrical stretching of the rubber at a const. rate, with examn. by the microscope. Various types of rubber, including frozen samples, were examd., the influence of the rate of stretching, the temp., the degree of mastication and the state of vulcanization being detd. and correlated with the accompanying changes in mech. properties. In place of the theory of Hauser and Mark, according to which the appearance of x-ray interferences is due to crystals already present in coherent form, the hypothesis is advanced that the impurities form a coherent whole, out of which a crystallizable substance is expelled by stretching or by racking, which is purified to an extent that it can crystallize and become a discontinuous phase. Simple models can readily be made to illustrate the phenomenon. Among other features, the well-known differences in the "melting point" are easily comprehensible by the aid of this hypothesis. The Joule-Thompson heat effect is explained as a heat of crystn. and of fusion or soln. A general discussion follows the paper. C. C. DAVIS

**Rubber in the production of leather.** CRISPIN. *Gummi-Ztg.* **43,** 2534–5(1929).—A general discussion, with particular reference to certain recent patents. C. C. D.

**The degree of devulcanization and the valuation of reclaimed rubbers. Answer to H. Loewen.** EUGENIO LINDMAYER. *Kautschuk* **5,** 183–4(1929).—Further comments (cf. Loewen, *C. A.* **23,** 3373). C. C. DAVIS

**Latex.** ST. REINER. *Chem. App.* **16,** 96(1929).—A general discussion of the structure of latex, its coagulation, industrial uses and transportation. M. C. R.

**Berginization of crude rubber.** H. I. WATERMAN, R. H. DEWALD AND A. J. TULLENERS. *Erdöl u. Teer* **22,** 403–4(1929).—Samples of 150 g. first latex crepe were heated to 450° for 15 min. with and without an initial H pressure of 110 kg. per cm. With

max. pressures of 250 and 50 kg., resp., the results were: *C residue*, 0, 1.6%; *oil b.* < 220°; 43.8%, 39.9%; Br. no. 40, 34; $n_D^{20}$ 1.45, 1.46; aniline pt. 21°, 4°; *oil b.* 220–300°, 23.5%, 20.7%; Br. no. 13, 13; $n_D^{20}$ 1.502, 1.519; aniline pt. 23.5°, 4°.

A. W. FRANCIS

**Heats of combustion of rubber, gutta-percha and balata.** T. H. MESSENGER. *Trans. Inst. Rubber Industry* **5**, 71–86(1929).—It was thought that measurements of the heats of combustion of rubber, gutta-percha and balata might throw light on the unsettled problem of the difference in constitution of these 3 substances. At the same time, the effect of mastication on the heat of combustion of rubber was detd. The 3 substances were extd. with cold water, dried *in vacuo*, extd. with AcMe, dissolved in $C_6H_6$, filtered, pptd. with abs. EtOH, dissolved in $CHCl_3$, repptd. with AcMe, and extd. with boiling AcMe, then with water and finally dried, all the treatments being carried out in the absence of air. The combustions were made in an O bomb and calorimeter of standard type. The av. heats of combustions of rubber, gutta-percha and balata were 10,970, 10,990 and 11,000 cals. per g., resp., showing the close similarity in chem. properties of the 3 substances. Rubber was then disaggregated in 2 ways: (1) by mech. mastication, and (2) by exposure to sunlight, and the heats of combustion of the products were detd. in comparison with that of the original rubber. Though in each treatment the rubber was disaggregated to such an extent that the soln. viscosities in $C_6H_6$ were lowered to relatively insignificant values, the heats of combustion remained unaltered, showing that internal mol. changes (depolymerization) do not occur either during milling or exposure to sunlight, and that the changes observed are the result of phys. changes in the state of aggregation. A discussion of the *C/H ratio in rubber, gutta-percha and balata*, based on a survey of the literature, indicates the validity of the $C_5H_8$ ratio. The expts. of M. give the empirical formula $C_{10}H_{16.09}$ for balata.

C. C. DAVIS

**The permeability of rubber mixings.** W. CECIL DAVEY AND T. OHYA. *Trans. Inst. Rubber Industry* **5**, 27–30(1929).—Expts. on the relative permeability to H of vulcanizates contg. (1) rubber and S; (2) rubber, S, accelerator, ZnO; (3) rubber, S, accelerator, ZnO, stearic acid; (4) rubber, S, accelerator, ZnO, antioxidant; (5) rubber, S, accelerator, ZnO, softeners; and (6) rubber, S, accelerator, ZnO, stearic acid, and pigments or fillers, showed that the permeability is lower in accelerated than in unaccelerated mixts.; that it is lowered still further by softeners and by antioxidants; and that it is increased by mineral fillers. With the finest pigments, however, the increases are relatively small. Before curing, the permeability of the mixts. was much lower than after curing. An *app.* designed especially for measuring the permeability of rubber is described and illustrated.

C. C. DAVIS

**The aging of cotton contained in rubber goods.** GUY BARR. *Trans. Inst. Rubber Industry* **5**, 31–47(1929).—The article describes a variety of expts. which have been carried out by B. and by others in the past on the *natural and artificial aging of rubberized balloon fabrics*. Expts. on the *comparative effects of ultra-violet light and of tropical sunlight* showed that there are essential differences between the 2 effects. Losses in tensile strengths of the fabrics were similar, but though the permeability of the samples exposed to ultra-violet light remained the same, the samples exposed to sunlight became extremely permeable and their $H_2SO_4$ content became relatively large. Ultra-violet light caused disproportionately great deterioration of the cotton, whereas tropical sunlight acted relatively rapidly on the rubber and S, with formation of $H_2SO_4$, which in turn attacked the cotton. Since the phys. and chem. effects were so different in ultra-violet light and in sunlight, an ultra-violet light test is useless for foreseeing the behavior of rubberized fabrics in sunlight. Org. dyes and inorg. pigments afford protection on exposure of cotton to sunlight, $PbCrO_4$ giving the best results. Expts. in which unrubberized cotton was exposed to radiation of different wave lengths showed that deterioration occurred only in violet and in near-ultra-violet light and that filters which absorb all radiation below 4000 A. U. afford almost complete protection. A good idea of the efficiency of screens in absorbing from sunlight radiation injurious to cellulose may be had by comparing their behavior with Velox or other AgBr paper, max. deterioration of the cellulose occurring with the same radiation which causes the max. effect on AgBr. The deterioration of cotton in sunlight is essentially oxidation, the cotton acquiring the reducing properties of oxy-cellulose. Graphs show the losses of strength of cotton exposed for increasing times to 0.0005 *N*, 0.00025 *N* and 0.000125 *N* $H_2SO_4$, and then heated at 110°, 119° and 127°, resp., for 1–16 days. At a given temp. the rate of loss of strength was roughly proportional to the wt. of acid in the fabric. With a given acid content the rate of loss of strength doubled with an increase of temp. of 8°. A general discussion follows the paper.

C. C. DAVIS

**Some observations on carbon black.** C. M. CARSON AND L. B. SEBRELL. *Ind. Eng. Chem.* **21**, 911–4(1929).—By studying the adsorptive capacity for accelerator, the effects of heat, the reaction with S and ZnO and the dispersion (rate of settling) of different types of C black, it was possible to correlate their behavior in these respects with their effects in vulcanized rubber. The adsorptive capacity is a measure of the rate of vulcanization of rubber mixts. contg. the blacks, C blacks with low adsorptive capacities giving faster curing mixts. than blacks with high adsorptive capacities. Heating C blacks to 500–1200° rendered them highly adsorptive, and also made the rubber mixts. contg. them vulcanize faster and have higher moduli than the same mixts. contg. the corresponding unheated blacks. With S and ZnO in boiling xylene, C blacks liberate a substance having an accelerating action. An indication of the stiffening action of a C black may be had by detg. in a thin rubber cement the quantity which is dispersed to an extent where it cannot be centrifuged out again under definite conditions. C. C. D.

**Comparison of acetylene black with gas black and lamp black.** T. R. DAWSON AND N. H. HARTSHORNE. *Trans. Inst. Rubber Industry* **5**, 48–70(1929).—Systematic expts. were carried out to compare the phys. and chem. properties of 2 American gas blacks, 2 lamp blacks and a Canadian acetylene black, and their effects in different proportions in unaccelerated and in accelerated rubber mixts. The comparative analyses of their phys. and chem. properties are described in detail. In unaccelerated mixts., gas black was intermediate in behavior between acetylene black and lamp black, except for tensile strength and reënforcing power, in which respects the gas blacks and acetylene black were almost the same. In properties related to strength, such as rigidity, absorption of energy and hardness, the gas and acetylene blacks were relatively close together, with the lamp blacks showing considerably different properties. In properties related to elasticity, such as permanent set and resilience, the gas blacks approached the lamp blacks, the acetylene black standing apart. The following data give the % difference from the lamp black in the tensile strength, elongation at 0.75 kg. per sq. mm., rigidity (kg. at 300% elongation), energy absorption, permanent set, hardness and resilience of the gas blacks and the acetylene black, resp.: 26, 23; —3, —11; 20, 34; 40, 40; 50, 120; 25, 35; —3, —9. The results show that each type of C black has advantages for certain definite purposes. When comparing blacks of distinctly differing types, tensile strength, energy absorption, permanent set and hardness are most useful, while in comparing blacks of similar type or in detg. the variability of a single black, elongation, rigidity, permanent set and resilience (those properties which differ greatly) are most useful. Permanent set is recommended as a particularly useful criterion. In accelerated mixts. the gas blacks were again intermediate in effects between the lamp blacks and acetylene black, approaching more nearly acetylene black. With the accelerated mixts. there was very little leveling of the differences found among the blacks in the unaccelerated mixts., which is contrary to general belief. The lamp blacks had a relatively great weakening effect on the activity of the accelerators, and this to a degree which varied with the individual accelerator. An investigation of the variation in successive lots of the same acetylene black showed that the differences in quality may be as great as the differences between gas black and acetylene black, but that they are smaller than those between lamp black and acetylene black. A general discussion follows the paper. C. C. DAVIS

**The use of Thénard blue in accelerated rubber mixtures.** RUDOLF DITMAR AND HEINZ PREUSSE. *Gummi-Ztg.* **43**, 2749–50(1929).—Thénard blue is stable during S vulcanization without accelerators, in $S_2Cl_2$ vulcanization either as vapor or in $CS_2$, in vulcanization by ultra-violet light, and in vulcanization with S in air. It shows compatibility with most accelerators, though it activates some (*e. g.*, the butyraldehyde condensate of dimethyl-*p*-phenylenediamine) and cannot be used with others (*e. g.*, aldehyde-ammonia). It cannot be used for coloring hard rubber. C. C. DAVIS

**Titanium white or lithopone?** ERICH WURM. *Gummi-Ztg.* **43**, 2752(1929).—Expts. during the past 3 yrs. by W. do not support the contention that $TiO_2$ is more economical than lithopone in rubber. Based on the relative costs and coloring power lithopone is the more economical, and furthermore vulcanizates contg. lithopone age considerably better than the corresponding vulcanizates contg. $TiO_2$, particularly with products cured with $S_2Cl_2$. Examn. of $TiO_2$ from different sources showed that all contained traces of Ti. It is considered that lithopone is much preferable to $TiO_2$ as a white pigment for rubber goods. C. C. DAVIS

**The coloring of rubber.** G. MARTIN. *Rev. gén. mat. color.* **32**, 213–9(1928).—The dyeing of rubber in bulk and by surface coloring is discussed, together with the methods of application and dyes suitable for each. ROBERT HOUGHTON

**Studies on the hydrogen-ion concentration by coagulating latex of Hevea brasiliensis. I. Sodium fluosilicate as coagulating agent.** L. R. VAN DILLEN. *Arch. Rubbercultuur* **13**, 448–64(1929). (In briefer form in English 465–72.)—The beginning of a

study of the $p_H$ concn. at which latex coagulates, the present paper deals with the theory of the quinhydrone electrode and the system used in the exptl. work undertaken. The assumption of van Harpen regarding the splitting of $Na_2SiF_6$ is discussed critically and is considered to be erroneous. An alternate theory is offered in its place. $Na_2SiF_6$ soln. acts as a buffer, the components being 1 part of NaF and 2 parts of HF. The $p_H$ values of the $Na_2SiF_6$ solns. are higher than the theoretical values of the corresponding buffer mixts., but NaF and HF in $Na_2SiF_6$ solns. are available in very low concns. By dilg. a buffer consisting of 1 equiv. of NaF and 2 equivs. of HF, the $p_H$ value is the same as in $Na_2SiF_6$ soln. By dilg. a $Na_2SiF_6$ soln. the $p_H$ value diminishes at first and subsequently increases gradually. This may be explained on the assumption that the degree of hydrolysis increases more rapidly than the degree of diln. At the lowest $p_H$ value the remaining fluosilicate is entirely split up, after which by carrying on to a greater diln. the concn. of NaF and of HF diminish, and this involves a gradual increase of the $p_H$. Tests with very weak mixts. of latex and $Na_2SiF_6$ solns. showed that in this way the $p_H$ values diminished greatly, chiefly as a result of the remaining fluosilicate splitting up entirely though there are probably other phenomena contributing to this result. Moreover, by dilg. with water samples of latex of different origins, great differences in the $p_H$ range were found, because of the fact that the water samples were buffered in a different way. Measurements of the $p_H$ values in buffers consisting of NaF and HF proved the assumption that in $Na_2SiF_6$ solns. 1 mol. of $Na_2SiF_6$ yields 1 mol. of NaF and 2 mols. of HF. C. C. DAVIS

**Uses of rubber latex.** JOSEPH ROSSMAN. *India Rubber World* **81,** No. 1, 63–6 (1929).—A survey of U. S. patents dealing with the direct applications of latex in industry. C. C. DAVIS

**Observations on the chemical constitution and physical properties of rubber.** LOTHAR HOCK AND GUIDO FROMANDI. *Rubber Chemistry and Technology* **2,** 365–6 (1929).—English version of *C. A.* **23,** 3371. C. C. DAVIS

**The "freezing" of raw rubber.** A. VAN ROSSEM AND J. LOTICHIUS. *Rubber Chemistry and Technology* **2,** 378–83(1929).—English version of *C. A.* **23,** 2320. C. C. DAVIS

**Determination of the iodine number of raw rubber.** ADOLF GORGAS. *Rubber Chemistry and Technology* **2,** 362–4(1929).—English version of *C. A.* **23,** 1525. C. C. DAVIS

**Rubber compounding practice. Ingredients for economy, processing and inflation.** WEBSTER NORRIS. *India Rubber World* **81,** No. 1, 53–6(1929); cf. *C. A.* **22,** 2489.—The discussion includes barytes, whiting, dusting powders, kerosene and sponging agents. C. C. DAVIS

**Toxic substances in the rubber industry. I. Benzene.** P. A. DAVIS. *Rubber Age* (N. Y.) **25,** 367–8(1929).—The results of an examn. of 7000 patients during 12 yr. are described. **II. Carbon tetrachloride.** *Ibid* 483–4. **III. Aniline.** *Ibid* 611–2. C. C. DAVIS

**The recovery of volatile solvents in the rubber industry.** ANON. *India Rubber World* **81,** No. 1, 57(1929).—An illustrated description of the "Acticarbone" process. C. C. DAVIS

**The purification and fractionation of rubber. VII.** RUDOLF PUMMERER, ALBRECHT ANDRIESSEN AND WOLFGANG GÜNDEL. *Rubber Chemistry and Technology* **2,** 367–72(1929).—English version of *C. A.* **22,** 4873. C. C. DAVIS

**The absorption of oxygen by rubber.** G. T. KOHMAN. *Rubber Chemistry and Technology* **2,** 390–405(1929).—See *C. A.* **23,** 2600. C. C. DAVIS

**The tackiness of unvulcanized rubber.** T. L. GARNER. *Rubber Chemistry and Technology* **2,** 384–9(1929).—See *C. A.* **23,** 3373. C. C. DAVIS

**The preparation and molecular size of isorubber nitrone. VIII.** RUDOLF PUMMERER AND WOLFGANG GÜNDEL. *Rubber Chemistry and Technology* **2,** 373–7(1929).—English version of *C. A.* **22,** 4874. C. C. DAVIS

**Transformation of energy by rubber.** IRA WILLIAMS. *Ind. Eng. Chem.* **21,** 872–6 (1929).—The exptl. data indicate that elasticity is a property which persists through vulcanization and is not created by the latter process. The phys. state of the rubber after any cure depends upon the balance between suppression of plasticity (caused directly or indirectly by the reaction with S) and the creation of plasticity by heat. Moreover S probably combines at a slower rate with the elastic component so that a product with almost no mech. strength is finally formed. The transformation of energy by rubber depends upon the condition of the rubber as well as the conditions of the test. Heat liberated by elastic strain can be transformed almost quantitatively into mech. work. Heat arising from internal frictional resistance caused both by plastic and by elastic flow is irreversible. Any reduction in time of transfer of energy reduces the

quantity lost through plastic flow, while an increase of temp. increases the resistance of the elastic component to strain, but also reduces the resistance of the plastic component to flow. With sufficient increase of temp., there is a large loss of energy because of a considerable though limited permanent flow of the rubber. This cannot be plastic flow of the elastic component since it is limited in magnitude, and it can be explained by a mech. change, *e. g.*, a breaking of the anchorage between the plastic substance and the elastic network. C. C. DAVIS

**Accuracy of rubber stress-strain determinations.** W. H. STEVENS. *India Rubber J.* **78,** 380(1929).—A comparison of the frequency distribution of tensile strength values obtained by Wiegand and Braendle (*C. A.* **23,** 4372) with those of de Vries (cf. *Estate Rubber*, 466; *C. A.* **15,** 2563) shows a resemblance between the 2 sets of data, including a similar neg. skew. The conditions of testing were different in the 2 cases, so that it is difficult to judge the significance of this similarity. C. C. DAVIS

**The double refraction of stretched rubber.** W. C. VAN GEEL AND J. G. EYMERS. *Rubber Age* (N. Y.) **25,** 491–3(1929).—English version of *C. A.* **23,** 4099. C. C. DAVIS

**The relationship between forces and deformations, with special reference to rubber.** R. ARIANO. *India Rubber J.* **78,** 316–8(1929).—English version of *C. A.* **23,** 545. C. C. DAVIS

**Pigment reënforcement.** R. W. LUNN. *Rubber Chemistry and Technology* **2,** 409–20(1929).—See *C. A.* **23,** 3371. C. C. DAVIS

**Comparison between Vulkan DK Red and Selenium Red.** R. DITMAR AND K. H. PREUSSE. *Caoutchouc & gutta-percha* **26,** 14686(1929).—Selenium Red (**I**) is stable with all com. accelerators, whereas Vulkan DK Red (**II**) gives attractive red colors only with Zn ethylphenyldithiocarbamate, cyclohexylamine dithiocarbamate, mercaptobenzothiazole and thiocarbanilide. **I** is stable with soap or with EtOH, whereas **II** is not. In general **I** can be used for a much greater variety of purposes than can **II**. C. C. D.

**Why not have more sponge rubber products?** R. R. OLIN. *Rubber Age* (N. Y.) **25,** 663–4, 673(1929).—An illustrated description showing the present status of the sponge rubber industry and its future possibilities. C. C. DAVIS

**Spray sulfur for rubber tree protection.** VINCENT SAUCHELLI. *India Rubber World* **81,** No. 1, 65(1929).—A com. type of S is described which has a particle size of 4–15$\mu$, and which is extremely effective for combating fungous diseases when used in the regular manner. It should also be of value in *vulcanizing latex.* C. C. DAVIS

**The reclaimed rubber industry in the United States today.** ANON. *Rubber Age* (N. Y.) **25,** 554–8(1929).—Numerous illustrations of plants are included. C. C. D.

**An enquiry into the use of reclaimed rubber.** J. PANEM. *Déchets et régénérés* **1,** No. 2, 2(1929); cf. Hutchinson, *C. A.* **23,** 4373.—Satisfactory results in manuf. can be obtained with reclaimed rubbers only by the use of types which are uniform and which show good aging properties. C. C. DAVIS

**The history and trends in the use of reclaimed and scrap rubber.** H. A. WINKELMANN. *Rubber Age* (N. Y.) **25,** 544–7, 561(1929).—Descriptive. C. C. DAVIS

**The rational use of scrap and reclaimed rubber.** H. BAUFARON. *Rev. gén. caoutchouc* **6,** No. 54, 13(1929).—Typical formulas contg. large proportions of scrap or reclaimed rubber for various uses are given. C. C. DAVIS

**Classification of reclaimed rubbers.** W. E. GLANCY. *Rubber Age* (N. Y.) **25,** 560(1929).—The different types of reclaimed rubber now in use are distinguished, with accompanying data showing the usual limits of acetone ext., $CHCl_3$ ext., ash, d. and tensile strength (no formula or conditions are given) of tire, tire friction, solid tire, inner tube and boot and shoe reclaimed rubbers. C. C. DAVIS

**Reminiscences of an old timer in the reclaimed industry.** L. J. PLUMB. *Rubber Age* (N. Y.) **25,** 552–3, 562(1929).—A general description, showing the chem. and technical developments which have taken place. C. C. DAVIS

**Effect of milling on the plasticity of reclaimed rubber.** D. P. SWISHER AND P. W. SANDERS. *Rubber Age* (N. Y.) **25,** 559–60(1929).—An exptl. comparison was made between the plasticizing effect of milling for various lengths of time on (1) tire reclaim alone; (2) a mixt. (50:50) of reclaim and pale crepe and (3) pale crepe alone. Plasticity measurements were made, after cooling 3 hrs., with the Williams app. at 70°. The results are given graphically and in tables. Milling had less effect on the plasticity of reclaimed rubber than it did on raw rubber, and yet a mixt. of raw and reclaimed rubber was more easily plasticized on milling than was raw rubber alone, confirming previous observations that reclaimed rubber aids in the plasticizing of new rubber. After reclaimed rubber formed a solid sheet on the mill, little further diminution in plasticity took place, the only effect of continued milling being to increase the stickiness decidedly. This latter effect makes the use of reclaimed rubber particularly advantage-

ous in frictioning mixts. where skimming from the roll is to be avoided. Judged by tensile product, continuous milling did not impair the phys. properties of reclaimed rubber or of the mixt. of reclaimed and new rubber to any considerable extent. C. C. DAVIS

**Plasticizers, plastics and plasticity.** PAUL BARY. *Plastics* **5**, 497–9(1929).—See *C. A.* **23**, 2849. E. M. SYMMES

**Rubber cements and adhesives.** S. D. SUTTON. *India Rubber World* **81**, 58–9 (1929).—An illustrated description. C. C. DAVIS

**The manufacture of tennis shoes.** H. BAUFARON. *Déchets et régénérés* **1**, No. 2, 5–6(1929).—Formulas contg. reclaimed rubber for use in making different colors and types of shoes are suggested. C. C. DAVIS

**An attempt at a rational classification of the principal accelerators of vulcanization.** G. MARTIN AND R. THIOLLET. *Rubber Chemistry and Technology* **2**, 356–61(1929).—English version of *C. A.* **23**, 4101. C. C. DAVIS

**The identification of accelerators in [rubber] mixtures by means of ultra-violet radiation.** M. L. P. *Rev. gén. caoutchouc* **6**, No. 53, 9–12(1929).—By irradiation of rubber mixts. contg. accelerators with ultra-violet light, the different fluorescent colors and tones of color observed make it possible to identify the particular accelerator which is present (cf. Kirchhof, *C. A.* **22**, 2291, 2855). Characteristic colors are also obtained after vulcanization, though they are different from the corresponding ones before vulcanization. If the color of a control rubber mixt. is compared with that of a doubtful rubber mixt., it is possible in mfg. operations to ascertain whether or not an accelerator is present in the doubtful mixt. With the *app.* which is described and illustrated, not only may the identity of the accelerator be established but also its approx. quantity within a precision of ±5%. Ultra-violet radiation is filtered through $CuSO_4$ soln. or other suitable filter; it is then reflected on the unknown and on the control sample, then passes through a screen which forms a pencil of light for each sample, next through a cell contg. triphenylmethane, and finally the pencils of light are reflected by means of silvered glass into the eye-piece. To det. the quantity of accelerator, pencils of light from control samples contg. different known proportions of accelerator are passed through a prism, the position of which is thereby calibrated to correspond to each proportion of accelerator. C. C. DAVIS

**The mode of action of organic accelerators. II.** PAUL BARY. *Rev. gén. caoutchouc* **6**, No. 53, 3–5(1929); cf. *C. A.* **23**, 4373.—A further discussion, including vulcanization without S. C. C. DAVIS

**The nature of vulcanization. IV.** H. P. STEVENS AND W. H. STEVENS. *Rubber Chemistry and Technology* **2**, 421–8(1929).—See *C. A.* **23**, 3596. C. C. DAVIS

**Developments in a new process of vulcanizing rubber goods.** HENRY R. MINOR. *Rubber Age* (N. Y.) **25**, 613–4(1929).—Substantially the same as *C. A.* **22**, 1705. C. C. DAVIS

**The problem of vulcanization without sulfur.** LEO ECK. *India Rubber J.* **78**, 354, 356(1929).—English version of *C. A.* **23**, 4847. C. C. DAVIS

**Further information on surface vulcanization in the quartz light.** R. DITMAR AND O. GRÜNFELD. *Gummi-Ztg.* **43**, 2801–3, 2859–61(1929).—In continuation of earlier expts. (cf. D., *C. A.* **23**, 4374), exptl. data show the effects obtained with various accelerators, activators and Vulkan colors in rubber mixts. vulcanized by ultra-violet light. Surface vulcanization by the latter radiation is unquestionably a true vulcanization process, since it was proved that S must be present and that the S is activated by the radiation and then enters into reaction with the rubber. Since ultra-violet light is a very active catalyst, activator and accelerator of surface vulcanization when about 3% S is present, effecting cures in very short times, the addn. of org. accelerators can be completely dispensed with. Most org. accelerators have an unfavorable action. In most cases, Vulkan colors gave excellent shades of color under these conditions, and in combination with other inorg. and org. colors, such as Se red or methylene blue, all kinds of colors and tones can be obtained. In general vulcanization with ultra-violet light can be effected in 4–8 min. at 20–90°, depending upon the support on which the sample rests, the shortest times being obtained on glass. This influence of the support apparently depends upon its heat cond. and heat capacity, for the higher the temp. prevailing during the vulcanization in ultra-violet light the more rapid is the rate of the latter. C. C. DAVIS

**The oxidation of vulcanized rubber.** A. VAN ROSSEM AND P. DEKKER. *Rubber Chemistry and Technology* **2**, 341(1929).—English version of *C. A.* **23**, 2598. C. C. D.

**The effect of solvents on the stress-strain curve of vulcanized rubber.** A. H. TILTMAN AND B. D. PORRITT. *India Rubber J.* **78**, 345–6(1929).—The work is of importance because rubber products often come in contact with org. solvents either during

or after manuf. Samples of a vulcanizate, the compn. of which was smoked sheet 57, S 3, $Ca(OH)_2$ 0.5, ZnO 39.5 (cured 3.25 hrs. at 280°F.), were exposed at room temp. to $C_6H_6$ vapor for various times to obtain different proportions of absorbed $C_6H_6$, and were then tested (1) immediately, and (2) after drying to the original wt. The results indicate that the rigidity of vulcanized rubber is diminished considerably by the absorption of small proportions of solvent. Thus at 600% elongation the absorption of 5% (by wt.) of $C_6H_6$ lowered the rigidity by 21%. The greatest effect was obtained with the first 20–30% of absorbed $C_6H_6$, further absorption having a less marked effect on the stress-strain curve. The absorption of $C_6H_6$ had little effect on the ultimate elongation, whereas the tensile strength was lowered considerably. This is, however, probably not true of rubber swollen by immersion in liquid, where absorption is far greater. Absorption followed by complete drying produces a slight, technically negligible, permanent effect on the stress-strain curve. The expts. show that when a solvent must be used, either during manuf. or subsequently, the solvent should be as free as possible from components with high b. ps. All stresses were calcd. on the dimensions of the original dry rubber, and therefore the low rigidity of swollen rubber cannot be ascribed merely to a "diln." of the rubber by absorbed liquid, but must be a result of a loosening of the cohesive forces among the ultimate particles. C. C. DAVIS

**Effect of temperature on the acetone extract of vulcanized rubber exposed to sunlight.** T. YAMAZAKI. *Caoutchouc and gutta-percha* **26**, 14691(1929).—On exposure to sunlight in summer, the acetone ext. of undercured rubber became greater than that of the corresponding rubber when overcured, whereas in winter the contrary was true. The mixt., rubber 92.5, S 7.5, was cured to different degrees and the vulcanizates were then exposed for 100 hrs. to sunlight at 10–5° and at 50–60°, and in another series at approx. 20° and at 60–70°. In each series the acetone exts. increased and the free S decreased far more rapidly at the higher than at the lower temps., and the differences were similar to those obtained in summer and in winter. Therefore the differences obtained in summer and in winter are attributable to differences in temp. rather than to differences in the intensity of the sunlight. C. C. DAVIS

**Some preliminary experiments on the causes of the deterioration of ebonite when exposed to light and air.** J. D. FRY AND B. D. PORRITT. *India Rubber J.* **78**, 307, 309–10(1929).—On the assumption that the increase in the elec. cond. of hard rubber by exposure to light and air is a result of the formation of a surface film contg. acids, expts. were carried on to ascertain the mechanism of this phenomenon. It was found that $H_2S$ is evolved, the rate of evolution being the greatest in direct sunlight, perhaps, however, because of temp. rather than of light effects. This evolution of $H_2S$ results from decompn. of the rubber-S compd., and occurs in the absence of free S, resins, O and water vapor. The rate of evolution increases with increase of temp. C. C. DAVIS

## Patents

**Centrifugal concentration of latex.** AKTIEBOLAGET SEPARATOR. Brit. 304,686, Jan. 24, 1928. Liquid to be treated is supplied from a tank of uniform cross section in which the surface is protected from the air by a float which prevents evapn. of $NH_3$ or other preservative. Various other app. details are described.

**Composition from rubber latex and casein.** WM. W. CHRISTMAS. U. S. 1,724,906, Aug. 20. Casein is dissolved in a strong $NH_3$ soln. heated to about 70–90°, mixed with raw rubber latex, and the resulting compn. is dried and vulcanized.

**Rubber.** ERNST ROHLIN. Ger. 478,590, Aug. 23, 1925. A dipping app. for the prepn. of rubber goods and for the recovery of the solvent is described.

**Preserving rubber.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 305,195, Feb. 2, 1928. Aryl hydroxides such as hydroquinone and amines such as aniline are caused to react in the absence of solvents (suitably by heating with $CaCl_2$) to form compds. which improve the "aging qualities" of rubber. Cf. *C. A.* **23**, 4376.

**Preserving rubber.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 305,572, Feb. 7, 1928. The "aging qualities" of rubber are improved by adding aromatic nitrosoamines such as the nitroso derivs. of phenyl-β-naphthylamine, β,β-dinaphthylamine or the like.

**Preserving rubber.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 305,647, Feb. 9, 1928. See U. S. 1,717,093 (*C. A.* **23**, 3828).

**Retarding deterioration of rubber.** WM. S. CALCOTT, WM. A. DOUGLAS and OLIVER M. HAYDEN (to E. I. Du Pont de Nemours & Co.). U. S. 1,725,564, Aug. 20. In order to retard deterioration by the action of oxidation and heat, there is incorporated with rubber 2 or more substances such as *m*-toluylenediamine and phenyl-α-

naphthylamine, one of which primarily retards deterioration by action of heat and the other of which primarily retards deterioration by the action of O.

**Rubber pastes.** I. G. FARBENIND. A.-G. Brit. 305,490, Feb. 3, 1928. A paste which can be homogeneously mixed with fillers, vulcanizing agents, etc., is prepd. from natural or synthetic latexes or the like by treatment with a water-sol. cellulose ether such as the methyl ether or a soln. of the ether, heating to form a ppt. and sepg. the ppt. from the water. Various details are given.

**Extrusion method for making rubber inner tire tubes.** HERMAN T. KRAFT (to Goodyear Tire & Rubber Co.). U. S. 1,724,354, Aug. 13. An app. and various details of procedure are described.

**Forming rubber tire tubes by extrusion.** DUNLOP RUBBER CO., LTD., and F. FELLOWES. Brit. 305,152, Oct. 31, 1927. Mech. features.

**Forming seamless rubber tires, etc., by deposition on the surface of a hollow mold.** J. TOWNLEY. Brit. 304,633, Oct. 21, 1927. Mech. features.

**Cleaning rubber molds.** G. G. ANDREWS (to Goodyear Tire & Rubber Co.). Brit. 305,531, Feb. 6, 1928. Alk. solns. are used under heat and pressure, *e. g.*, NaOH, KOH or Na sulfide may be used under a steam pressure of about 80 lb. per sq. in. An app. is described.

**Coloring rubber and similar materials.** IMPERIAL CHEMICAL INDUSTRIES, LTD., A. J. HAILWOOD, W. J. S. NAUNTON and A. SHEPHERDSON. Brit. 304,376, Oct. 21, 1927. Materials such as rubber, balata or gutta-percha are colored by incorporating with them a pigment consisting of a vat dye and a finely divided substratum substantially insol. in water. Various details and examples are given.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 304,207, Jan. 16, 1928. Coagulation of a synthetic latex such as may be formed from isoprene and Na oleate soln. is effected by cooling to below 0°, and after thawing the coagulum is sepd. from the aq. emulsifying and polymerizing agent. Unpolymerized diolefin present is removed by heating or reduced pressure, use of a gas current or by rolling the coagulum. Several examples are given. Cf. *C. A.* **23**, 2324.

**Synthetic rubber compositions.** I. G. FARBENIND. A.-G. Brit. 304,612, Jan. 20, 1928. Sheets or other forms of material for use in the same manner as linoleum, celluloid, horn, etc., are made from synthetic rubber (such as that from isoprene) with an artificial or natural resin or other plastic material and org. or inorg. fillers or both. Factis, natural rubber, cellulose esters or ethers, dyes, etc., may be included in various compns.

**Rubber vulcanization accelerators.** SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,724,180, Aug. 13. Polynitrophenylbenzothiazyl sulfides (and corresponding chlorophenyl compds.), details of the production of which are given, are accelerators of the vulcanization of rubber. They all have antioxidant properties and improve the aging of rubber, and particularly is this true of the 2,4-dinitrophenylbenzothiazyl sulfide. The 2,4,6-trinitrophenylbenzothiazyl sulfide, which may be also called picrylbenzothiazyl sulfide, has the property of improving the flexing of a rubber compd.

**Chlorinating rubber.** F. C. DYCHE-TEAGUE. Brit. 305,968, Sept. 13, 1927. Rubber is first "disaggregated" or depolymerized by continued mastication until the "nerve" is completely destroyed, and is then chlorinated. The mastication may be effected in $CCl_4$ accompanied by exposure to ultra-violet rays; prior to mastication the rubber may be exposed to air or $O_3$ to effect oxidation.

**Treating rubber with chlorostannic and chlorostannous acids.** H. A. BRUSON (to Goodyear Tire & Rubber Co.). Brit. 306,390, Feb. 18, 1928. Tough balata-like products or ebonite-like products (depending on the time and temp. of heating) are obtained. The corresponding Br acids also may be used.

**Uniting rubber and cellulose derivatives.** C. MACINTOSH & CO., LTD., S. A. BRAZIER and G. F. THOMPSON. Brit. 305,745, Dec. 1, 1927. Mutual solvents of rubber and of the cellulose derivs. are used as bonding agents. Various details are given.

**Ornamental embossing of rubber sheets.** BROADHURST & CO., LTD., and W. J. DEXTER. Brit. 306,276, Feb. 11, 1928. Mech. features.

**Use of sponge rubber and ordinary rubber in forming rubber brushes, etc.** F. A. LEESON and L. A. KOHLER. Brit. 305,735, Nov. 21, 1927. Structural features.

**Sealing containers with rubber latex.** B. DEWEY (to DEWEY & ALMY CHEMICAL Co.). Brit. 306,040, Feb. 14, 1928. The rubber particles of a latex are vulcanized while conserving the aq. suspension as described in Brit. 193,451 (*C. A.* **17**, 3430) and the water is evapd. after application of the latex as a sealing material. Bentonite or other materials may be added.

**Devulcanizing scrap rubber.** DUNLOP RUBBER CO., LTD., D. F. TWISS and F.

THOMAS. Brit. 305,826, Feb. 17, 1928. Scrap rubber is treated at atm. pressure with a hot soln. of caustic alkali in a polyhydric alc. such as glycerol until it can be sheeted.

**Apparatus for testing the strength and elasticity of cords.** M. L. KOCHHEISER and S. A. STEERE (to Goodyear Tire & Rubber Co.). Brit. 306,555, Feb. 23, 1928. Structural features.

**Plastic compositions.** JEAN BAER. Swiss 132,322, Oct. 15, 1927. Elastic rubber-like bodies sol. in $CS_2$ are prepd. by the action of HCHO on S or polysulfides in the presence of a solvent.

**Plastic compositions.** JEAN BAER. Swiss 132,505–132,508, Oct. 20, 1926. Rubber-like masses are prepd. by the action on S or polysulfides of $C_2H_4Br_2$ (132,505), $C_2H_4I_2$ (132,506), $CH_2Cl_2$ (132,507) or $CH_2Br_2$ (132,508) in the presence of a solvent. The products are sol. in $CS_2$.

**Concentrating latex, etc.** DUNLOP RUBBER CO., LTD., D. F. TWISS and E. A. MURPHY. Brit. 307,315, Nov. 3, 1927. Liquids such as latex, liable to suffer coagulation, skin formation or like changes during evapn., are concd. with or without admixt. of stabilizers, accelerators, preservatives, etc., in an app. which is described and which keeps the material in motion in a rotatable and oscillating receptacle having a temp.-regulating jacket. A latex mixt. to be concd. may be composed of rubber 71.6, S 2.5, accelerator 5, ZnO 2, Fe oxide 3, mineral oil 7, whiting 6, china clay 6.7, oleic acid 0.2, casein 0.1 and KOH 0.4 part.

**Reversible concentrated latex.** PAUL SCHOLZ. U. S. 1,729,522, Sept. 24. A reversible concd. latex contains about $^1/_8$–$^1/_2$% of salicylic acid or a salicylate. Small proportions of KOH, K soap, etc., also may be added.

**Composition comprising latex or other rubber dispersions.** DUNLOP RUBBER CO., LTD. and R. C. DAVIES. Brit. 306,621, Dec. 1, 1927. Finely divided fillers such as "gas black" are dispersed in an aq. or slightly alk. soln. of cellulose xanthate, for incorporation in latex, etc., which may be vulcanized. Other compounding ingredients may be added to the xanthate or latex.

**Rubber.** I. G. FARBENIND. A.-G. Fr. 658,757, May 5, 1928. Inorg. salts of dithiocarbamic acids sol. in water, are used as *accelerators* in the vulcanization of natural or artificial rubber.

**Natural and synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 307,375, Dec. 5, 1927. Rubber is coagulated from emulsions of synthetic rubber or mixts. of these with natural lattices, by use of proteolytic enzymes. Various details and examples are given.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Brit. 307,308, March 3, 1928. In polymerizing butadiene or similar hydrocarbons, the polymerization is conducted in successive stages with intermediate interruptions at which further addns. of the same or a different hydrocarbon to be polymerized may be made. Various details and examples are given. Cf. *C. A.* **23,** 4848.

**Synthetic rubber.** I. G. FARBENIND. A.-G. Fr. 658,652, Aug. 7, 1928. Rubber is obtained by polymerizing butadiene hydrocarbons in the presence of other hydrocarbons such as butylene which do not take part in the polymerization. If the butadiene is obtained by the heat decompn. of a hydrocarbon, other hydrocarbons forming by-products of the reaction need not be sepd., *e. g.*, hexamethylene gives a mixt. of butadiene and butylene.

**Artificial rubber.** I. G. FARBENIND. A.-G. Fr. 658,359, July 19, 1928. Artificial rubber or masses resembling rubber are made by cautiously heating hydrocarbons such as butadiene or isoprene with substances having a "hydrotopic" action, such as salts of sulfonic or carboxylic acids and their substitution products, amides and other substances having a like action, in aq. emulsion, with or without emulsion colloids such as albumin compds. Cf. *C. A.* **23,** 4103.

**Desulfurizing rubber.** ARMAND ROGER. Fr. 659,480, Dec. 16, 1927. Waste vulcanized rubber, preferably freed from free S, is desulfurized by heating it with a divided adsorbent material such as active charcoal, $SiO_2$ gel or infusorial earth. A substance such as metallic Na capable of combining with the S or a vulcanization accelerator such as diphenylguanidine may be added to the adsorbent.

**Isomerizing rubber.** B. F. GOODRICH CO. Brit. 307,134, Dec. 20, 1927. A heat-plastic product suitable for use with various solvents in coating compns., etc., is obtained by heating rubber in the presence of a solvent such as $C_6H_6$ with PhOH and a strong non-oxidizing inorg. acid such as HCl or a sulfonic acid or sulfonyl chloride. The product may be directly used for coating metals by neutralizing the acid present (suitably by $NH_3$). Cf. *C. A.* **23,** 4007.

**Electrophoretic deposition of rubber.** S. E. SHEPPARD and C. L. BEAL (to Anode Rubber Co., Ltd.). Brit. 307,585, Jan. 21, 1928. The heat produced by passage

of the current is removed by artificial cooling, enabling a high current d. to be employed. Numerous details of app. and procedure are described.

**Retarding aging of rubber.** A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 307,013, March 1, 1928. Substances such as phenylaminobenzyl alcs. and *p*-*α*- or -*β*-naphthylaminobenzyl alcs. (the manuf. of which is described) are used as "anti-agers."

**Rubber solutions for use as adhesives.** H. O. BRUHN. Brit. 306,864, Nov. 24, 1927. Solns. suitable for uniting woven materials comprise rubber dissolved in $CCl_4$ or similar C or hydrocarbon halide to which may be added a perfume and a substance for rendering the soln. more viscid such as an aq. soln. of sulfate of Al, Mg or Zn, $Ca(NO_3)_2$, Na Al chloride or the Na salt of propylnaphthalene sulfonic acid.

**Rubber compositions.** DUNLOP RUBBER CO., LTD., and R. C. DAVIES. Brit. 306,994, Dec. 1, 1927. Cellulose xanthate gel is added to latex or other rubber or similar dispersions to form compns. for molding, producing *leather-like products*, etc., with fillers, coloring substances, vulcanizing agents, etc.

**Rubber compositions.** IMPERIAL CHEMICAL INDUSTRIES, LTD., A. J. HAILWOOD, W. J. S. NAUNTON and A. SHEPHERDSON. Brit. 307,155, Jan. 11, 1928. Dispersion of fillers, dyes, accelerators, etc., in rubber is facilitated by coating finely divided particles of the material to be dispersed with substances such as oils, fatty acids, paraffin or other rubber softeners (which in some cases may combine with the material, as when stearic acid is used with magnesia). The material may be first formed into cakes and then ground.

**Rubber compositions.** AMERICAN GLUE CO. Fr. 659,368, Aug. 23, 1928. See U. S. 1,683,862 (*C. A.* **22**, 4274). Fr. 659,369. See U. S. 1,683,863 (*C. A.* **22**, 4274).

**Freeing mercury from rubber compositions.** BERNARD ORMONT (to Keystone Chemical & Mfg. Co.). U. S. 1,728,359, Sept. 17. In order to free chem. combined Hg from a matrix contg. rubber the material is heated sufficiently to melt the rubber, and further heated to a higher temp. completely to vaporize the combined Hg; the combined vapor is subjected to condensation to recover Hg and rubber as a condensate, the latter is heated to vaporize the Hg and rubber, and the product is washed with xylene to remove the rubber. An app. is described.

**Rubber composition for making paving blocks, etc.** EDMOND DRAULLETTE. U. S. 1,728,990, Sept. 24. Soft rubber waste 20–40, hard rubber waste 65–25 and fatty residues 15–35% are mixed and plasticized by heating to 120–150°. U. S. 1,728,991 relates to structural features of paving blocks formed in part of rubber compn.

**Rubber-coating fabric-covered electrical conductors.** EDGAR W. ENGLE (to Fansteel Products Co.). U. S. 1,729,160, Sept. 24. Fabric-covered conductors are dipped into a weak soln. of rubber, partially dried, then dipped into a strong soln. of rubber and the rubber is vulcanized on the conductor.

**Coating metal or other surfaces with rubber.** DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 307,180, Feb. 8, 1928. The surface is first covered with gauze or mesh (stuck to the surface at intervals) and a soln. or aq. dispersion of rubber is then applied. Drying and vulcanizing may be concurrently effected.

**Joining rubber and metal surfaces.** S. S. K. JUNIOR (to Goodyear Tire & Rubber Co.). Brit. 307,056, March 2, 1928. Steel or other metal surfaces to which rubber is to be joined are preliminarily treated with salts of Co and Cu such as the oleates, stearates, palmitates, acetates or chlorides, or a rubber cement contg. Co or Cu salts may be used. Various details and modifications of procedure are described.

**2,6-Dinitro-4-chlorophenyldialkyldithiocarbamates.** SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,726,648, Sept. 3. These compds. (*rubber vulcanization accelerators*) are made by treating a soln. of a metallic dialkyldithiocarbamate (*e. g.*, Na dimethyldithiocarbamate) with 2,6-dinitro-1,4-dichlorobenzene, heating, cooling and crystg. and washing free from sol. chlorides.

**Phenylmethylenebisdialkyldithiocarbamates.** SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,726,647, Sept. 3. A soln. of a dialkyldithiocarbamate salt (*e. g.*, the dimethyl) is treated with benzal chloride, heating is continued until the benzal chloride has substantially disappeared, the reaction mixt. is cooled and the phenylmethylenebisdialkyldithiocarbamate is sepd. by crystn. Products of this character may be used as *rubber vulcanization accelerators*.

**2,4-Dinitrophenyl dithiocarbamates.** SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,726,646, Sept. 3. Polynitrophenyl disubstituted dithiocarbamates are made by treating a soln. of a salt of a disubstituted dithiocarbamate with a soln. of a dinitrochlorobenzene. These compds. are sol. in $C_6H_6$, acetone and hot alc. and may be used as *accelerators in vulcanizing rubber*.

**Vulcanizing rubber.** CLAYTON O. NORTH and CHESTER W. CHRISTENSEN (to Rubber Service Laboratories Co.). U. S. 1,726,713, Sept. 3. See Fr. 652,817 (*C. A.* **23**, 3600).

**Vulcanizing rubber coverings of metal rolls by electric heating.** C. MACINTOSH & Co., LTD. and H. W. WOLTON. Brit. 307,628, March 10, 1928. A current of low voltage and high amperage may be passed through the metal spindle, or, with hollow rolls, a Cu coil may be inserted and an a. c. passed through it.

**Treating latex.** JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,730,518, Oct. 8. A resin solvent in which rubber is substantially insol., *e. g.*, a dil. alc., and an alk. material such as $NH_3$ are added to latex, which is maintained in uncoagulated state and given increased mechanical stability. Latex thus treated is suitable for coating, impregnation, etc. Numerous examples are given. Cf. *C. A.* **23**, 3375.

**Treating rubber latex.** ERNEST A. HAUSER (to K. D. P., Ltd.). U. S. 1,729,651, Oct. 1. In producing a compounded product contg. all the solid and dissolved constituents of the original latex and in which the latex is still in a reversible condition, protective agents are added to the latex and it is concd. by evapn. until a completely reversible colloidal paste-like product is obtained, compounding and vulcanizing ingredients are gradually mixed with it and are uniformly dispersed and compounded while conserving the colloidal properties and stability of the latex towards friction, pressure, agitation, etc., by effecting and continuing the mixing with the least possible friction. The product is suitable for squirting, pressing or molding.

**Rubber composition.** CHARLES H. CAMPBELL (to American Glue Co.). U. S. 1,729,709, Oct. 1. A metal albuminate such as that of Fe is mixed with rubber before vulcanization and serves to improve its durability.

**Rubber compositions.** MERWYN C. TEAGUE (to Naugatuck Chemical Co.). U. S. 1,730,485, Oct. 8. In order to improve the union between rubber and pulverulent materials such as clay or lampblack, the latter are evacuated and treated with $NH_3$ gas in the presence of moisture so that the gas is adsorbed on and serves to peptize the material and the latter is then combined with the rubber. Cf. *C. A.* **23**, 1527.

**Rubber-like composition.** JOHN C. WICHMANN (to Cactus Rubber Co. of America). U. S. 1,730,702, Oct. 8. A product which is suitable for use as a rubber substitute comprises a rubber-like material resulting from the boiling of the concd. juice of cactus in assocn. with Na tungstate, Na molybdate, boiled linseed oil and rubber dissolved in turpentine, and drying and oxidizing.

**Apparatus for calendering rubberized cord fabric.** JOHN F. HOGAN (to B. F. Goodrich Co.). U. S. 1,730,657, Oct. 8. Structural features.

**Artificial flowers comprising united layers of sheet rubber.** STEWART H. ROGERS. U. S. 1,730,628, Oct. 8. The marginal edges of the rubber are cemented together and stiffening material such as paper or cloth is placed between the rubber layers.

**Rubber-coated fabric suitable for ornamenting cloth.** MATTHEW LINDENBERG. U. S. 1,730 665, Oct. 8. Cloth is coated with rubber cement, a coating of powdered rosin is applied to the cement, the latter is dried, another coating of the rubber cement is applied and dried, and a layer of gutta-percha is applied to the cement-coated surface.

**Reclaimed rubber.** CHARLES H. CAMPBELL (to American Glue Co.). U. S. 1,729,706, Oct. 1. Rubber scrap is devulcanized by a process of hydrolytic character, in which the material is subjected to the action of cleavage products obtained from collagen. U. S. 1,729,707 specifies cleavage products of keratin instead of those of collagen. U. S. 1,729,708 relates to reclaimed rubber having cleavage products from the hydrolytic decompn. of ox blood compounded with it by an alk. process having a hydrolytic action which renders the ox blood and its hydrolyzed products sol.

**Vulcanizing hose.** ERNEST BLAKER (to B. F. Goodrich Co.). U. S. 1,730,639, Oct. 8. Hose is distended against an exterior confining device by maintaining a distending fluid such as water under pressure within the hose during vulcanization, and the hose is cooled in distended condition by maintaining a cooling fluid under pressure within the hose while causing it to flow through the latter. An app. is described.

[Translated from Gazzetta Chimica Italiana, Vol. 59, No. 8, pages 550–552, August, 1929.]

# Quebrachitol from the Serum of Hevea Latex

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It is a well-known fact that quebrachitol (*levo*-methylinositol) is present in high proportion in the serum of the latex of *Hevea brasiliensis*. By concentrating *in vacuo* the serum of latex to 2.5 per cent of its original weight and leaving this concentrate exposed to the air for many days, Contardi[1] obtained crude quebrachitol. This he purified by dissolving it in boiling water and decolorizing it with bone black. Left to itself, there separated from the solution pure quebrachitol. By treating the mother liquors with 1:10 sulfuric acid for 5 to 6 hours at a pressure of 15 atmospheres, neutralizing with barium carbonate, and allowing to crystallize, Contardi obtained a total of more than 350 g. of pure quebrachitol from 36 kg. of serum or 54 kg. of latex. I have noticed that the separation of quebrachitol from latex serum and still more so from the serum of slab rubber (a maturated rubber obtained by leaving the coagulum in the serum for several days) can be carried out more rapidly, and a higher yield obtained, than by the more costly method mentioned above if the procedure described below is followed.

From the latex serum ready for evaporation on a water bath, the proteins are precipitated by tannic acid, using 5 g. of tannin per kilogram of serum. The evaporation is then carried on until all water is eliminated and the residue is dissolved in an equal weight of glacial acetic acid. Solution is complete, and from the solution quebrachitol crystallizes out with a yield of 12.5 g. per kg. of serum. The quebrachitol thus obtained is practically pure.

With serum from slab rubber, it is not even necessary to precipitate the proteins with tannic acid because in this serum they are no longer present or rather they have been transformed in other substances during the maturation process. With serum from slab rubber it is sufficient during the evaporation on the water bath to filter the magnesium ammonium phosphate, which separates in considerable quantity during the concentration of slab rubber serum, then to dissolve in glacial acetic acid the residue from the evaporation. By warming gently, solution is complete, and on cooling pure quebrachitol (m. p. 187°) separates and may be readily filtered. The yield of pure quebrachitol is 12 g. per kg. of serum.

Three new esters of quebrachitol were prepared. Contardi[2] has already prepared quebrachitol acetate from quebrachitol and acetic anhydride. Moldavskii[3] has recently prepared various esters of inactive inosite by the reaction of the latter with aliphatic acid chlorides. He describes the hexa-isovalerate $(C_4H_9COO)_6C_6H_6$ with m. p. 137° and the hexapalmitate $(C_{15}H_{31}COO)_6C_6H_6$ with m. p. 75°. I have prepared these same esters and have found that the hexa-isovalerate fuses at 151° C. and the hexapalmitate at 83° C. Evidently the esters prepared by Moldavskii were not pure.

The new esters of quebrachitol which were prepared included the following three: *Quebrachitol penta-isovalerate* $(C_4H_9COO)_5C_6H_6OCH_3$. This was prepared by refluxing 1.95 g. of quebrachitol with 6.10 g. of isovaleryl chloride. It is liquid at the ordinary temperature.

*Quebrachitol pentalaurate* $(C_{11}H_{23}COO)_5C_6H_6OCH_3$. This was prepared by heating *in vacuo* at the temperature of the reaction (120° to 160° C.) a mixture of 1.95 g.

of quebrachitol and 11 g. of lauryl chloride. The product of the reaction crystallized from alcohol fuses at 32° C.

Analysis: Found—C 72.11%, H 11.16%, $OCH_3$ 2.68%; calculated—C 72.82, H 11.23, $OCH_3$ 2.81.

*Quebrachitol pentapalmitate* $(C_{15}H_{31}COO)_5C_6H_6OCH_3$. This was prepared by heating *in vacuo* at the temperature of the reaction (120° to 160°) a mixture of 1.95 g. of quebrachitol and 14 g. of palmityl chloride. The product of the reaction crystallized from alcohol fuses at 58° C.

Analysis: Found—C 75.14%, H 11.88%, $OCH_3$ 2.12%; calculated—C 75.43%, H 11.84%, $OCH_3$ 2.24%.

## Summary

A new procedure for the separation of quebrachitol from the serum of the latex of *Hevea brasiliensis* is described, and three new esters of quebrachitol are prepared.

## References

[1] *Ann. chim. applicata*, **14**, 281 (1924).
[2] *Ibid.*
[3] *J. chim. Ukraine*, **1**, 408 (1925).

[From Transactions of the Institution of the Rubber Chemistry, Vol. 5, No. 2, pages 95–116, August, 1929.]

# The Swelling of Vulcanized Rubber in Liquids

J. R. Scott

*Introduction.*—The object of this paper is to present some of the results of an investigation of the swelling of vulcanized rubber carried out in the laboratories of the Research Association of British Rubber Manufacturers. It would be impossible in the space available to describe all the work in detail, and what follows must be regarded merely as a summary of the outstanding results obtained, supplemented by references to published literature.

The mechanism of the absorption of liquid and the structure of swollen rubber gels are not discussed in this paper; water absorption also is omitted, as it depends mainly on the non-rubber constituents, and therefore differs essentially from the absorption of organic liquids.

*Experimental Method.*—Swelling was measured by immersing a piece of rubber (volume about 1 cc.) in the liquid at a constant temperature, usually 25° C. (34° C. has since been found more convenient). Exposure to light was avoided during the test [see Section 5, paragraph (*b*)]. The increase in weight of the rubber was taken as the weight of liquid absorbed; this weight, together with the specific gravities of the rubber and liquid, was then used to calculate the swelling, *i. e.*, the volume of liquid absorbed expressed as a percentage of the volume of the original rubber.

This method is *a priori* open to certain objections: (i) The weight increase equals the weight of liquid absorbed *minus* the weight of soluble matter extracted; as the rubbers contained no appreciable soluble matter other than rubber resin and free sulfur, the quantity of matter extracted could not vary sufficiently from rubber to rubber or from liquid to liquid to introduce serious errors; removing the soluble matter, *e. g.*, by a preliminary acetone extraction, is objectionable because the heating involved alters the properties of the rubber. (ii) The method is not accurate with liquids which are mixtures of components of different densities and swelling capacities, because the absorbed liquid differs in composition, and therefore in density, from the bulk; in such cases it may be preferable to determine the volume of the swollen rubber directly, *e. g.*, by weighing in air and in water, and to take the difference between this volume and that of the original rubber as the volume of absorbed liquid; of the many liquids examined (see Table I) it was only found necessary to adopt this method in the case of petrol.

It was shown experimentally with some fifteen liquids that the volume of swollen rubber was sensibly equal to the sum of the volumes of the original rubber and the absorbed liquid, after allowing for the soluble matter extracted; in other words, the swelling process involves no increase or decrease (at any rate greater than 1 or 2 per cent of the volume of the rubber) in the total volume of the system. This result agrees with the findings of Tompkins (*Discussion on Colloids; Faraday and Physical Societies*, London, **1920,** 177). Posnjak (*Koll. Chem. Beihefte*, **3,** 417 (1912)) observed a volume decrease of 1 per cent during the swelling of raw rubber.

## 1. The Time-Swelling Curve

It is one of the characteristics of vulcanized rubber, as distinguished from raw rubber, that it absorbs liquids such as benzene, carbon disulfide and petroleum hydrocarbons without losing its shape, becoming sticky, or dissolving to any appreciable extent; also, the absorption of liquid practically ceases after a certain

time, whereas with raw rubber it continues rapidly until the rubber dissolves. Nevertheless, it is not true to say that the swelling of vulcanized rubber proceeds only up to a definite limiting value, as is commonly supposed; in reality, a very slow absorption of liquid continues indefinitely, as shown by the time-swelling curve (O E A B) in Fig. 1.

The time-swelling curve consists of two portions: the markedly curved position O E A, representing the initial rapid absorption of liquid, and the final part A B which is almost straight and has a slight upward slope, representing a slow continued absorption of liquid, which will be termed the "swelling increment" (the slope is exaggerated in Fig. 1). The existence of this increment does not appear to have been recorded previously, although time-swelling curves showing the effect have been obtained (*e. g.*, by Kirchhof, *Koll. Chem. Beihefte*, **6**, 1 (1914)).

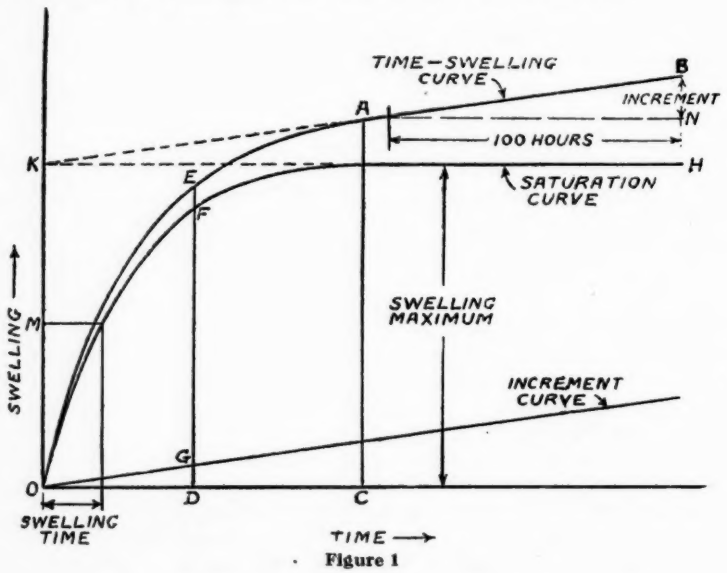



**Figure 1**

The important characteristics of the increment are: (i) With most rubbers and liquids it takes place at an approximately constant rate. (ii) It continues indefinitely; experiments have been carried on until the rubber became too flabby to handle (nearly a year) without any sign of the absorption of liquid ceasing. (iii) When the curves for different liquids or for different rubbers are compared, the rate of increment, *i. e.*, the slope of A B, is found to be independent of the height A C and horizontal length O C of the initial part of the curve. (iv) The increment can be considerably increased or decreased by external agencies without appreciably affecting the initial absorption O E A (see Section 3).

These characteristics show that the increment is not merely a very slow approach to a maximum swelling, but is a definite characteristic property of the rubber-liquid system. For purposes of quantitative examination, therefore, the swelling process may be considered as the resultant of two distinct processes going on simultaneously: (*a*) a simple saturation of the rubber with liquid, proceeding to a maximum value (O K) and then stopping, as shown by the "saturation curve" O F H in Fig. 1; (*b*) a very slow, practically uniform increase in swelling, or "increment," which must be ascribed to some progressive change in the properties of the rubber,

and may be represented by the "increment curve," which is a straight line starting from the origin and parallel to A B. The time-swelling curve is therefore the "sum" of the saturation and increment curves, in the sense that any ordinate E D of the time-swelling curve equals the sum of the corresponding ordinates D F, D G of the saturation and increment curves.

With all the rubbers and liquids yet examined it has been found that if rubber test-pieces of the same dimensions are used, the saturation curves are, to a first approximation, all derivable from a single parent curve by multiplying its ordinates and abscissae by appropriate factors characteristic of each rubber–liquid system, in other words, by merely altering the time and swelling scales. Consequently, any saturation curve is completely defined by the equation to the parent curve together with two parameters—the height, representing the amount of liquid absorbed, and the length, representing the time factor.

The complete time-swelling curve can therefore be expressed in terms of four factors:

(i) *Swelling Maximum.*—The maximum height of the saturation curve (O K). This represents the swelling capacity of a given liquid for a given rubber. It is evident from Fig. 1 that the point K can be obtained by extrapolating the straight part A B of the time-swelling curve back to the swelling axis.

(ii) *Swelling Time.*—This represents the velocity factor in the saturation process. Theoretically, complete saturation requires an infinite time, so that the swelling time cannot be defined as the time required to reach this state. It may, therefore, be considered for comparative purposes as the time required to reach a given fraction of the saturation value, *e. g.*, $1/2$ as shown in Fig. 1, where O M = $1/2$ O K; it is obviously immaterial what fraction is chosen provided the same is always used. Swelling times measured in this way are of course purely relative numbers.

(iii) *Saturation Equation.*—No satisfactory equation has yet been found for the saturation curve. Several authors have proposed equations for the time-swelling curve, which usually closely resembles the saturation curve (Tompkins, *loc. cit.;* Flusin, *Ann. Chim. Phys.*, (8), **13,** 480 (1908); Bary, *Compt. rend.*, **161,** 589 (1915); Kirchhof, *Gummi-Ztg.*, **38,** 237 (1924); see also Kirchhof, *Koll. Chem. Beihefte,* **6,** 1 (1914); and Salkind, *Ber.*, **59** [B], 525 (1926); *Le Caoutchouc,* **23,** 13345 (1926)), but the results obtained in the present investigation do not accurately fit any of these equations.

(iv) *Increment.*—This may be defined as the increase in swelling per 100 hours on the straight part of the time-swelling curve, that is, B N in Fig. 1. With some rubbers the increment is not strictly a constant, but shows a very gradual decrease lasting for perhaps 1000 hours, after which it becomes constant and sometimes tends finally to increase. Occasionally, a gradual increase takes place from the start. The significance of these changes has not yet been investigated.

From the evidence at present available it appears that the increment is caused by a gradual depolymerization[1] of the rubber brought about by the atmospheric oxygen dissolved in the swelling liquid. The evidence for this view is as follows: (i) The increment shows no apparent relationship to the swelling maximum nor to the mechanical properties of the rubber, as would be expected if the increment resulted from a slow mechanical stretching of the rubber under the influence of the internal

[1] The term "depolymerization" is used throughout this paper to denote that alteration in rubber commonly attributed to the breaking down of larger into smaller structures. As the nature of this alteration is not definitely known, it is impossible to decide whether "depolymerization" (*i. e.*, breaking down of molecules) or "disaggregation" (breaking down of colloid particles) is the more appropriate. The use of the term "depolymerization" is not intended to exclude the possibility that the alteration may be one affecting colloidal particles rather than molecules.

swelling pressure. (ii) The polymerization involved in vulcanization is accompanied by a decrease in swelling, and the depolymerization (reversion) due to overcuring is accompanied by an increase; hence it is reasonable to assume that depolymerization in general increases the swelling—a conclusion which, incidentally, is in harmony with the theory that swelling depends on the osmotic pressure of the rubber molecules. (iii) The increment is greatly increased by adding to the swelling liquid agents which cause or accelerate depolymerization, *e. g.*, acids, salts of copper and manganese, or by exposure to light or high temperature in presence of air (see Sections 3 and 5); this confirms the explanation of the increment as being due to depolymerization. (iv) The increment is increased by oxidizing agents and decreased by antioxidants or by exclusion of oxygen (see Section 3); this shows that the increment is essentially the result of an oxidation process.

### 2. Influence of the Nature of the Swelling Liquid

Table I gives the swelling properties at 25° C. of the liquids examined; the rubber used was a 95:5 rubber-sulfur mixing cured to optimum mechanical properties (vulcanization coefficient 4.54).

TABLE I

| Liquid | Swelling Maximum | Swelling Time[8] | Increment |
|---|---|---|---|
| Benzene | 498 | 92 | 9.0 |
| Toluene | 504 | ... | .. |
| Xylene[1] | 501 | 101 | 7.6 |
| ψ-Cumene | 498 | 143 | 2.4 |
| Tetralin[2] | 564 | 370 | 17.9 |
| Dekalin[3] | 510 | 360 | 19.0 |
| Petroleum ether[4] | 234 | ... | .. |
| Petrol[5] | 389 | 98 | 8.4 |
| Paraffin oil[6] | 303 | 460 | 1.0 |
| Turpentine | 483 | 390 | 69.0 |
| Cyclohexane | 458 | 150 | 3.6 |
| Chloroform | 651 | 71 | 24.0 |
| Carbon tetrachloride | 659 | 133 | 8.9 |
| Carbon disulfide | 583 | 42 | 18.0 |
| Nitrobenzene | 145 | 400 | 3.8 |
| Aniline | 14 | ... | 0.1 |
| Anisole | 323 | 163 | 3.4 |
| Cyclohexanone | 158 | ... | .. |
| Cyclohexanol | 50 | ... | 11.0 |
| Cyclohexyl acetate | 307 | ... | .. |
| Methyl hexalin[7] | 90 | ... | 9.0 |
| Amyl acetate | 237 | 168 | 13.0 |
| Ethyl ether | 243 | 39 | 3.0 |
| Glycerine | 0 | ... | .. |

[1] Commercial "rectified" (mainly *m*-xylene).
[2] Commercial tetrahydronaphthalene.
[3] Commercial decahydronaphthalene.
[4] B. p. 50–60° C.; spec. grav. at 25° C.: 0.655.
[5] B. p. 70–170° C.; spec. grav. at 25° C.: 0.743.
[6] B. p. 180–280° C.; spec. grav. at 25° C.: 0.800.
[7] Commercial hexahydro-*p*-cresol.
[8] With a rubber disc 16 mm. diameter and 5 mm. thick, the time required to reach the point A on the time-swelling curve (see Fig. 1) is roughly equal to the swelling time expressed in hours.

(*a*) *Swelling Maximum.*—Consideration of the data in Table I shows that the swelling maximum is determined by the chemical character of the liquid rather than by its physical properties, as has already been pointed out by Kirchhof (*Koll.*

*Chem. Beihefte*, **6**, 1 (1914)), Salkind (*Ber.*, **59** [B], 525 (1926)) and Whitby (*Colloid Symposium Monograph*, Vol. IV, New York, **1926**, 203).

The following generalizations may be stated: (i) All hydrocarbon liquids have high swelling capacities; this agrees with Whitby's statement that non-polar liquids are good swelling agents for Rubber (*Can. Chem. Met.*, **9**, 265 (1925); *Chem. & Ind.*, **47**, 266 (1928)). (ii) Cyclic, *i. e.*, aromatic, hydroaromatic, and terpenic hydrocarbons have a greater swelling capacity than aliphatic hydrocarbons of similar molecular weight (compare benzene and its homologues and cyclohexane with petroleum ether, or tetralin and dekalin with paraffin). (iii) Unsaturation somewhat increases the swelling capacity (compare benzene with cyclohexane, or tetralin with dekalin). (iv) The halogen and sulfur substitution products of aliphatic hydrocarbons have unusually high swelling capacities in agreement with Le Blanc and Kröger's statement (*Kolloid-Z.*, **33**, 168 (1923)) that introduction of halogen or sulfur atoms increases the swelling power. (v) Substituents of a polar character, *e. g.*, nitro, amino, hydroxyl, and ketone groups, considerably lower the swelling capacity, as already noted by Whitby (*loc. cit.* [1925, 1926]; see also Cachtem, *Gummi-Ztg.*, **43**, 2099 (1929)); in some cases this effect is so pronounced that the swelling capacity is reduced to a negligible value or even eliminated, *e. g.*, aniline, glycerine. (vi) Esterification of a hydroxyl group increases the swelling capacity (compare cyclohexanol and cyclohexyl acetate). (vii) In a series of liquids containing the same polar group, swelling capacity increases with increasing molecular weight (Whitby, *loc. cit.* [1925, 1926]; Salkind, *loc. cit.*; Cachtem, *loc. cit.*); this is evident on comparing cyclohexanol with its methyl derivative methylhexalin. When a polar group is not present, this is not necessarily the case; for instance, benzene and its three homologues have approximately equal swelling capacities.

In groups of chemically similar liquids, *e. g.*, homologous series, the swelling capacity usually shows an inverse relationship to the dielectric constant (Le Blanc and Kröger, *loc. cit.*; Whitby, *loc. cit.* [1926]), although Salkind (*loc. cit.*) found no such relationship; Ostwald (*Kolloid-Z.*, **29**, 100 (1921)) claims the existence of such an inverse relationship for liquids in general, but this appears to be only of a very approximate nature (Le Blanc and Kröger).

The relative swelling capacities of different liquids depend to some extent on the nature of the rubber, particularly its combined sulfur content [see Section 4, paragraph (*b*)].

Mixtures of liquids generally have a greater swelling capacity than that calculated from their composition by the mixture rule, although occasionally the opposite is found, *e. g.*, with alcohol-ether mixtures (Mardles, *J. Chem. Soc.*, **127**, 2940 (1925)). For this reason, the addition to a swelling liquid, *e. g.*, benzene, of a second liquid, *e. g.*, alcohol, having little or no swelling action may increase the swelling, instead of producing a decrease as would have been expected; this effect has been fully investigated and its theoretical significance discussed by Tompkins (*Discussion on Colloids; Faraday and Physical Societies*, London, **1920**, 177).

Data on the swelling capacities of various liquids and mixtures are given in the following papers besides those quoted above: Flusin, *Ann. Chim. Phys.*, (8) **13**, 480 (1908); Boiry, *Le Caoutchouc*, **20**, 12010 (1923); Dubosc, *Le Caoutchouc*, **16**, 9781, 9813, 9815, 9845, 9847, 9850, 9852 (1919); Salkind (*loc. cit.*)has made an interesting comparison of isomeric esters.

(*b*) *Swelling Time.*—This property, unlike the swelling maximum, seems to be determined by the physical properties of the liquid, particularly its viscosity. The few results available (see Fig. 2) indicate an approximate proportionality between swelling time and viscosity, a relationship which might indeed be anticipated since swelling involves diffusion of liquid into the rubber; the dependence of rate of

swelling on viscosity has been mentioned (*e. g.*, by Salkind, *loc. cit.*, and Le Blanc and Kröger, *loc. cit.*), but no data for vulcanized rubber appear to have been published.

As some of the liquids included in Fig. 2 were mixtures or impure commercial products (dekalin, paraffin, petrol, tetralin, turpentine), the liquid absorbed by the rubber may have differed from the bulk; this may partly account for the deviations from a strict linear relationship.

It will be obvious from the foregoing considerations and from Table I that there is no direct relationship between the swelling maximum and the swelling time of a liquid. It can easily be shown that the initial rate of absorption of a liquid must be proportional to its swelling maximum divided by its swelling time. Consequently this initial rate cannot bear any fixed relationship to the swelling maximum, and

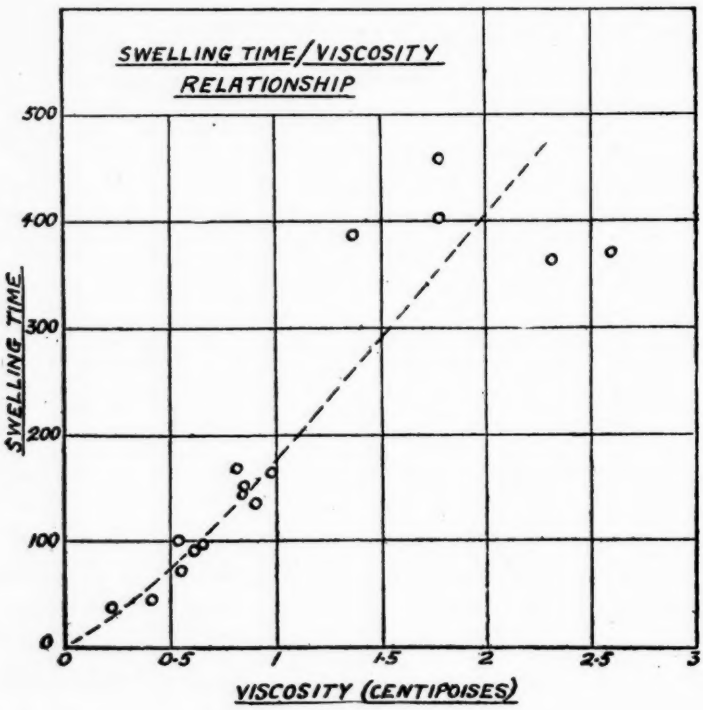



**Figure 2**

cannot, therefore, be a true measure of the swelling capacity of the liquid. This fact has been emphasized because in some investigations conclusions regarding the relative swelling capacities of different liquids have been based on measurements of the swelling after a comparatively brief period of immersion, which obviously represents the initial rate of absorption rather than the final maximum value.

(*c*) *Increment.*—This has not yet been found to bear any general relationship to the chemical or physical properties of the liquid. The very high increment of turpentine, however, is ascribable to its promoting, directly or indirectly, oxidation of the rubber by atmospheric oxygen.

### 3. Influence of Substances Added to Swelling Liquid

The swelling process is considerably influenced by adding to the liquid certain substances such as acids, bases, metallic salts, oxidizing agents, antioxidants, vulcanizing agents, and accelerators. A selection of results is shown in Table II; these figures refer to a 95:5 rubber-sulfur mixing (vulcanization coefficient 4.5) swelling in solutions of various substances in A. R. benzene at 25° C. Blank experiments with pure benzene were included to show the effect of the added substances on swelling maximum and increment; swelling time was not examined. In a few cases the increment decreased or increased as the experiment proceeded; in these cases (noted in the table) the initial value of the increment is given.

(*a*) *Swelling Maximum.*—The change in swelling maximum produced by the added substance is usually within the limits of experimental error imposed by the unavoidable inequalities in the rubber. Of the eight substances having apparently marked effects five give high increments which change with time, that is, the later part of the time-swelling curve is steep and not straight, so that the determination of the swelling maximum by extrapolating the curve back to zero time is attended with considerable uncertainty, and the apparent effect of the added substance may again be an experimental error.

In general, therefore, the swelling maximum is not appreciably affected by adding small amounts of substances to the swelling liquid. The increase with water, however, appears to be real, as it has been observed in other experiments; this increase

TABLE II

| Added Substance | Concentration Gr. per 100 Cc. | Relative Swelling Maximum[1] | Relative Increment[2] |
|---|---|---|---|
| Cupric oleate | 0.5 | 0.965 | 75+ |
| Manganous oleate | 0.5 | 1.00 | 3.3+ |
| Acetic acid | 1.0 | 1.005 | 1.02 |
| Chloroacetic acid | 1.0 | 1.06 | 4.85 |
| Trichloroacetic acid | 1.0 | 1.05 | 60− |
| Oleic acid | 1.0 | 1.00 | 1.4 |
| Aniline | 1.0 | 1.005 | 1.6 |
| Hydrazobenzene | 1.0 | 0.99 | 4.2− |
| Piperidine | 1.0 | 1.26± | 130− |
| Pyridine | 1.0 | 1.005 | 4.8 |
| Diphenylguanidine | 1.0 | 1.00 | 34− |
| *p*-Nitrosodimethylaniline | 1.0 | 1.055 | 103 |
| *p*-Nitrosodimethylaniline | 0.1 | 0.98 | 32 |
| Piperidine piperidine-1-carbothionolate | 1.0 | ? | About 80 |
| Tetramethylthiuram disulphide | 1.0 | 1.00 | 10.2 |
| Thiocarbanilide | 0.34* | 1.01 | 2.2 |
| Zinc ethylxanthate | 1.0 | 1.07 | 43− |
| Sulfur | 0.62* | 1.005 | 3.4 |
| *m*-Dinitrobenzene | 1.0 | 1.00 | 0.94 |
| 2,4,6-Trinitrotoluene | 1.0 | 1.01 | 1.2 |
| Benzoyl peroxide | 1.0 | ? | About 130 |
| Benzoyl peroxide | 0.1 | 0.97 | 140− |
| Turpentine | 1.0 | 0.995 | 7.5+ |
| Pyrogallol | 0.09* | 1.03 | 0.15 |
| Quinol | 0.07* | 1.005 | 0.15 |
| "Antox" | 0.5* | 1.01 | 0.40 |
| Rubber resin (crepe) | 0.9 | 1.005 | 0.55 |
| Rubber resin (smoked sheet) | 1.2 | 1.00 | 0.88 |
| Water | 0.06* | 1.03 | 0.68 |

[1] = (swelling maximum in solution) ÷ (swelling maximum in pure benzene).

[2] = (increment in solution) ÷ (increment in pure benzene). A minus sign denotes that the increment decreased during the experiment; a plus sign denotes an increase.

* Saturated solution.

may be due to absorption of water by the serum constituents, *e. g.*, sugars and proteins, present in the rubber.

(*b*) *Increment.*—The increment is increased by acids, organic bases, and salts of copper and manganese, that is, by substances which are generally considered to have a depolymerizing action on rubber. In the case of acids, the effect is greater the stronger the acid, as is shown by the series: acetic, chloroacetic, trichloroacetic. Oxidizing agents, *e. g.*, benzoyl peroxide, and substances which promote oxidation by atmospheric oxygen, *e. g.*, turpentine, also increase the increment (freshly distilled turpentine in absence of oxygen, however, does not), while antioxidants have the opposite effect. These facts are among those which have suggested the view that the increment observed with a pure liquid is mainly or entirely due to depolymerization of the rubber induced by atmospheric oxygen. This view is further supported by the fact that exclusion of oxygen considerably reduced the increment, as is shown by the following figures:

*95-Rubber-5-sulfur mixing (optimum cure) swollen at 34° C.*

| | Increment |
|---|---|
| 1. In benzene, with free access of air | 7.0 |
| 2. In air-free benzene; experiment made in a sealed evacuated vessel | 1.4 |

*Accelerators.*—All the organic accelerators examined increased the increment, some being extremely active in this respect. This indicates that accelerators depolymerize rubber, a result in agreement with the conclusions of other authors (Aultman and North, *India Rubber J.*, **1923,** 801; Le Blanc and Kröger, *Z. Elektrochem.*, **1921,** 335, *India Rubber World,* **1921,** 194; Ames, *J. Soc. Chem. Ind.*, **1924,** 117T; Naunton, *J. Soc. Chem. Ind.*, **1925,** 243T; Whitby, *Ind. Eng. Chem.*, **1923,** 1005). As vulcanization probably involves an initial depolymerization rendering the rubber reactive toward sulfur, one of the functions of an accelerator may be to hasten this depolymerization (see Le Blanc and Kröger, *loc. cit.* [1921]; Whitby, *loc. cit.* [1923]; Kirchhof, *Kolloid-Z.*, **1914,** 35; Twiss, *J. Soc. Chem. Ind.*, **1917,** 782; Ditmar, *Z. angew. Chem.*, **1921,** 465; *India Rubber World,* **1922,** 612). A comparison of accelerating and depolymerizing powers would therefore advance our knowledge of the mechanism of acceleration, and in this connection swelling tests might furnish useful indications of depolymerizing power.

*Vulcanizing Agents.*—The depolymerizing effect of sulfur, indicated by the increased increment, has already been observed in other ways (Aultman and North, *loc. cit.;* Le Blanc and Kröger, *loc. cit.* [1921]), and suggests that sulfur itself may promote the depolymerization necessary to vulcanization. As organic nitrocompounds have been claimed to act as vulcanizing agents, specimens of this class were included, but unlike sulfur they showed no appreciable depolymerizing effect.

*Rubber Resins.*—The resin of raw rubber resembled the antioxidants in reducing the increment; other experiments showed that the resin of vulcanized rubber behaved similarly. These results agree with the accepted view that rubber resins retard oxidation.

*Water.*—The reduction in increment produced by saturating the swelling liquid with water is in accord with the known effect of moisture in retarding the oxidation and deterioration of vulcanized rubber (see Stevens, *J. Soc. Chem. Ind.*, **1920,** 251T).

(*c*) *Swelling Time.*—According to Kirchhof (*Koll. Chem. Beihefte,* **1914,** 1), the resin and free sulfur normally present in vulcanized rubber increase the velocity of swelling, *i. e.*, reduce the swelling time.

In concluding this Section it should be emphasized that these experiments on the effect of added substances are only of a preliminary nature, serving to indicate the general character of the effects produced. The fact that the experiments were carried out without any precautions to exclude atmospheric oxygen probably com-

plicated the results in certain cases, for it is quite possible that a substance may have an intrinsic depolymerizing effect and at the same time retard depolymerization by acting as an antioxidant, so that the net result is the balance between two opposing effects.

### 4. Influence of the Nature of the Rubber

(*a*) *Time of Cure.*—With advancing cure the swelling maximum decreases, and in mixings with a low sulfur ratio (say, 5 per cent or less on the rubber) it reaches a minimum and then increases; this increase corresponds to the softening or "re-

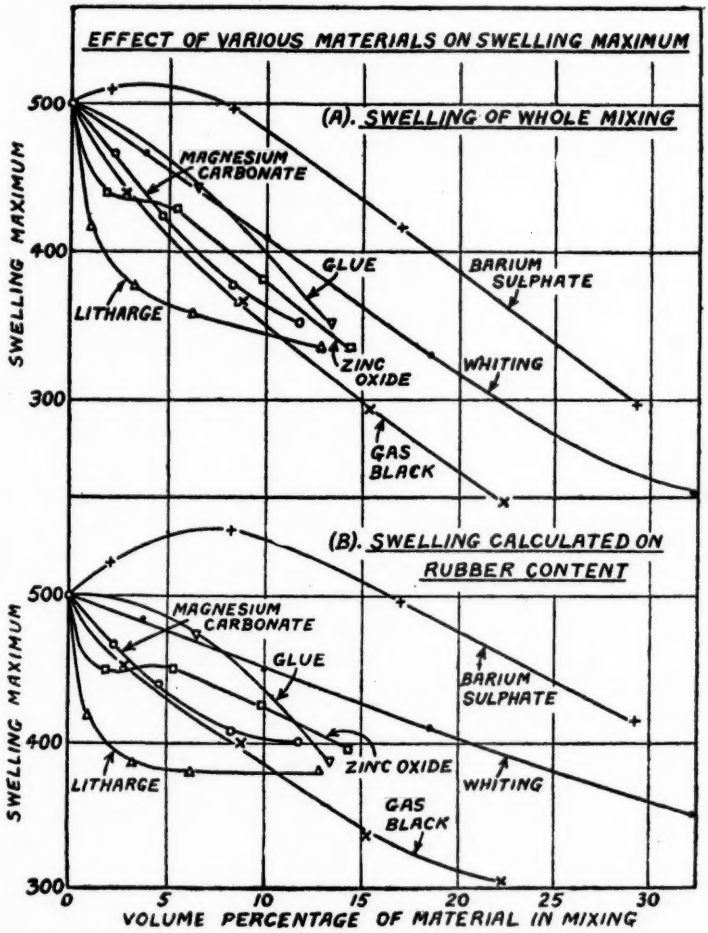



**Figure 3**

version" produced by overcuring; these facts have been noticed by previous workers (Kirchhof, *Gummi-Ztg.*, **1924,** 237; Stoll, *Gummi-Ztg.*, **1925,** 676). The minimum swelling coincides approximately with the minimum extensibility as measured by the elongation under a fixed load.

The swelling time and increment appear to change in the same way as swelling maximum, but this point has not yet been systematically investigated.

(*b*) *Composition of Mixing. Sulfur Ratio; Swelling of Ebonite.*—In mixings of a given type the minimum swelling (*i. e.*, the lowest obtainable in a range of cures) is lower the higher the sulfur ratio (Kirchhof, *Gummi-Ztg.*, **38,** (1924) 237). When the sulfur ratio is very high, as in ebonite, the swelling is reduced to a small fraction of that observed with soft rubber; thus, a 65-rubber-35-sulfur ebonite (combined sulfur 31 per cent) gave a swelling maximum of 69 in benzene at 34° C., as compared with 520 for a 95-rubber-5-sulfur mixing. The swelling time of ebonite on the other hand, is very much greater than for soft rubber, being of the order of 500 to 6000 compared with 100 for soft rubber. Penetration of liquid into ebonite is therefore a very slow process. Ebonite, like soft rubber, exhibits a swelling increment. A few experiments on the swelling of ebonite have been made previously (Boiry, *Le Caoutchouc*, **20,** (1923) 12010).

*Effect of Compounding.*—As the non-rubber constituents of a mixing do not in general absorb liquids, the swelling maximum is usually decreased by reducing the rubber content.

The effects of increasing proportions of typical ingredients, including inert fillers and reinforcing agents, are shown in Fig. 3; the basic mix consisted of rubber 95, sulfur 5, and all the mixings were cured to optimum mechanical properties, so that the swelling in each case was approximately the lowest obtainable with that particular mixing.

The swelling, calculated in the usual way as the volume increase of the sample (upper set of curves), in general decreased with increasing proportion of the added ingredient, and the reinforcing agents reduced the swelling more than did the inert fillers. The barium sulfate was exceptional in that small proportions increased the swelling. The relative effects of different materials varied according to the volume percentage added, litharge and zinc oxide being the most active in small quantities, while gas black was the most active when large quantities were used.

The effects of the various materials on swelling, including the abnormal behavior of small quantities of barium sulfate, were very similar to their effects on the extensibility of the rubber; this similarity is fully discussed in Section 6.

It is obvious that the addition of a non-swelling ingredient must lower the swelling by reducing the rubber content; in the lower set of curves in Fig. 3 this mere diluting effect has been eliminated by dividing the swelling by the rubber content (by volume) of the mixing, thus giving the percentage swelling of the actual rubber hydrocarbon. With the exception of small proportions of barium sulfate, all the materials evidently reduced the swelling of the rubber itself, the reinforcing agents again having the greatest effect. It is evident, therefore, that addition of non-rubber materials alters the swelling maximum not only by diluting the rubber but also by modifying its properties, usually in such a way as to reduce its swelling capacity.

Dubosc (*Le Caoutchouc*, **1917,** 9265) observed that the maximum swelling was reached more rapidly the lower the rubber content of the mix. This agrees with the present experiments, which showed that addition of compounding ingredients reduced the swelling time, there being indications of a proportionality between the swelling maximum and swelling time of different rubbers in the same liquid; this has not yet been investigated systematically.

The influence of compounding on the increment has not yet been examined.

*Accelerators.*—These have the same effect on swelling maximum as on extensibility, that is, for a given combined sulfur ratio the swelling is considerably reduced, a fact already noted by Kirchhof (*Gummi-Ztg.*, **1924,** 237); in some cases the reduction may be as great as 50 per cent. Broadly speaking, the reduction in swelling is greater the more active the accelerator, as would be expected according

to the view that accelerators reduce the depolymerizing effect of heat during the cure. Mixings accelerated with Vulcone have been examined by Stoll (*Gummi-Ztg.*, **1925,** 676).

*Antioxidants.*—These reduce the increment, just as they do when added to the swelling liquid (see Section 3); swelling maximum is not greatly affected.

*Influence of Composition on Relative Swelling Capacities of Different Liquids.*—The composition of the rubber affects to some extent the relative swelling powers of different types of liquids. This is mainly a question of the degree of vulcanization; thus, if the swelling capacity of benzene be taken as 100, the swelling capacities of petrol and paraffin decrease markedly with advancing cure, while those of xylene and carbon tetrachloride change only slightly; the figures in Table III, which are the mean results for several mixings, illustrate this point.

TABLE III

SWELLING CAPACITY RELATIVE TO BENZENE AS 100

| | Under-cure[1] | Optimum Cure |
|---|---|---|
| Petrol | 86 | 78 |
| Paraffin | 71 | 63 |
| Xylene | 104 | 102 |
| Carbon tetrachloride | 139 | 137 |

[1] Time of cure equal to half of that giving optimum cure.

The results of Boiry (*Le Caoutchouc*, **1923,** 12010) show very clearly this dependence on combined sulfur content: as the latter increases, the swelling capacities of all liquids decrease, but the decrease is most rapid with saturated hydrocarbon liquids, less rapid with aromatic hydrocarbons, and least rapid with liquids containing polar groups. The figures in Table III agree with these observations. When extreme variations in combined sulfur are encountered, as in comparing soft rubber with ebonite, the relative swelling capacities of two liquids may be reversed by the change in combined sulfur; thus, petrol swells soft rubber more than nitrobenzene (cf. Table I), but Boiry found that nitrobenzene has much the greater swelling action on ebonite.

Compounding ingredients have very little effect on the relative swelling capacities of different liquids (see Table IV), the few exceptional figures obtained being probably due to experimental errors.

TABLE IV

SWELLING CAPACITY RELATIVE TO BENZENE AS 100

| Added Ingredient[1] | Petrol | Paraffin | Xylene | Carbon Tetrachloride |
|---|---|---|---|---|
| (None) | 78 | 61 | 102 | 133 |
| Zinc oxide | 75 | 60 | 102 | 131 |
| Magnesium carbonate | 79 | 63 | 103 | 135 |
| Litharge | 82 | 64 | 102 | 147 |
| Whiting | 78 | 64 | 99 | 135 |
| Gas black | 77 | 61 | 98 | 129 |
| Barium sulfate | 70 | 60 | 99 | 131 |
| Glue | 80 | 64 | 106 | 139 |

[1] The compounded mixings contained 10 per cent by volume of the added material; basic mix, 95-rubber-5-sulfur.

It is evident that among ordinary soft rubbers the variation in composition does not markedly alter the relative swelling capacities of different liquids, so that in making comparisons of different rubbers (or liquids) it is immaterial what liquid (or rubber) is used, unless very accurate results are required.

*Mechanical Strength of Swollen Rubber.*—The composition of the rubber greatly influences its strength in the swollen condition. Little quantitative work has been

done on the mechanical properties of swollen rubber (see, however, Tiltman and Porritt, *India Rubber J.*, **1929,** 345), but hand tests have shown that rubbers having similar properties when dry may vary enormously in strength when swollen.

(*c*) *Effect of Aging. Swelling Maximum.*—During both natural and accelerated (Geer) aging the swelling maximum at first decreases, and then, after passing through a minimum value, begins to increase; this increase is sometimes followed by a second and final decrease; the initial decrease during aging was first noted by Kirchhof (*Gummi-Ztg.*, **1924,** 237). In every case yet examined the swelling changes have closely resembled the changes in the elongation under a constant load. The initial decrease in swelling is more pronounced (*i. e.*, the minimum reached is lower) in natural aging than during aging in the Geer oven.

*Swelling Time.*—This property appears to change in the same way as swelling maximum, these properties being roughly proportional. No systematic investigation has yet been made, however.

*Increment.*—The changes in increment appear, from the few results available, to differ according to the nature of the aging treatment. Experiments with rubber-sulfur mixings have shown that during natural aging the increment changes but little until the rubber begins to perish, when a rapid increase sets in, synchronizing with the fall in tensile strength and the rapid increase in weight, specific gravity, and acetone extract. During accelerated aging, as in the Geer oven, the increment first shows a considerable decrease, followed by an increase which, however, is much smaller than that observed during natural aging and does not always synchronize with perishing as indicated by the tensile properties.

It is evident from this result, and also from the swelling maximum changes mentioned above, that so far as swelling properties are concerned the Geer test does not exactly reproduce the changes caused by natural aging.

(*d*) *Influence of the Dimensions of the Rubber. Swelling Maximum.*—This, as would be expected, is not appreciably influenced by the dimensions of the rubber test-piece.

*Swelling Time.*—The swelling time increases with the size of the rubber, but the nature of the interdependence has not been systematically investigated except in the case of water absorption by rubber sheets, in which case the swelling time is proportional to the square of the thickness (Andrews and Johnston, *J. Amer. Chem. Soc.*, **46,** 640 (1924)). Some preliminary experiments have been made with rubber discs swelling in benzene, and the results indicate that the relationship noted by Andrews and Johnston applies also in this case.

*Increment.*—This also is affected by the form of the rubber, though to a much less extent than the swelling time (see Table V).

TABLE V

INCREMENTS OF RUBBER DISCS, 16 MM. DIAMETER, SWELLING IN BENZENE AT 25° C.

| | | | | | | |
|---|---|---|---|---|---|---|
| Solid tire rubber "A": | | | | | | |
| Thickness (cms.) | 0.123 | 0.306 | 0.485 | 0.65 | 0.92 | |
| Increment | 12.4 | 8.6 | 6.3 | 5.85 | 5.45 | |
| Solid tire rubber "B": | | | | | | |
| Thickness (cms.) | 0.046 | 0.082 | 0.175 | 0.274 | 0.453 | 0.745 |
| Increment | 5.4 | 4.75 | 3.75 | 3.55 | 3.3 | 3.2 |

In this case the ratio of the superficial area to the volume of the rubber seems to be the determining factor, the increment being approximately represented by the expression $a + bx$, where $x$ is the surface/volume ratio of the test-piece and $a$ and $b$ are constants.

It is evident that in experiments intended to be comparable, test-pieces of the same shape and size should be used, unless only the swelling maximum is required.

### 5. Influence of External Factors

(*a*) *Temperature.*—All three swelling properties are known to be dependent on temperature, although little has been done toward systematic investigation of the subject.

Swelling maximum increases with temperature, as already noted by Whitby (*Colloid Symposium Monograph*, Vol. IV, New York, **1926,** 203); the few data available give a temperature coefficient of 1.03 for a 10° C. rise in the neighborhood of 30° C. It is significant that this coefficient equals that which would be observed if swelling were proportional to the absolute temperature, namely 1.030.

The increment is much more sensitive, the temperature coefficient being about 2.5 for a 10° C. rise; the fact that this coefficient is roughly that of a chemical reaction lends support to the view that the increment results from depolymerization induced by oxygen.

The experiments of Kirchhof (*Koll. Chem. Beihefte*, **1914,** 1) show that the swelling time decreases with rise of temperature, as would be expected from the lowered viscosity of the swelling liquid.

(*b*) *Light.*—Exposure to light during the swelling process increases the increment; experiments on the same rubber, one carried out in darkness and the other in full daylight, gave increments of 2.4 and 5.7, respectively. The swelling maximum was not appreciably affected by the light.

(*c*) *Mechanical Pressure.*—Mechanical pressure, applied so as to resist the expansion of the rubber, reduces the amount of liquid absorbed (Graffe, *Le Caoutchouc*, **1927,** 13444; Hole, *Gas Journal*, **1923,** 504; **1924,** June 25; see *Rubber Age* (N. Y.), **1924,** 260). The relationship between the swelling and the applied pressure has not been investigated except in the case of raw rubber (Posnjak, *Koll. Chem. Beihefte*, **1912,** 417).

### 6. Relationship between Swelling and Other Properties of the Rubber

(*a*) *Swelling Maximum and Vulcanization Coefficient.*—In general, a high vulcanization coefficient is accompanied by low swelling (Graffe, *Le Caoutchouc*, **1927,** 13444; Boiry, *Le Caoutchouc*, **1923,** 12010), and Kirchhof (*Koll. Chem. Beihefte*, **1914,** 1) found that a simple mathematical relationship exists between vulcanization coefficient and swelling maximum for samples of the same mixing cured for different times.

(*b*) *Swelling and Mechanical Properties. Swelling Maximum.*—This is related to extensibility and hardness, a soft, easily extensible rubber always showing a high swelling, and *vice versa.* This relationship applies to all the factors which influence the properties of the rubber, such as time of cure, sulfur ratio, compounding, and aging. In a range of cures on one mixing Kirchhof (*loc. cit.*) found a simple mathematical relationship between swelling and elongation under a constant load.

Taking rubbers in general, however, the relationship between swelling maximum and mechanical properties is not mathematically exact. This is shown by plotting swelling maximum against elongation under constant load and against hardness for rubbers of different types, as in Fig. 4. Each curve represents the effect of adding increasing amounts of a given material to a basic mix of rubber 95, sulfur 5 (these rubbers are the same as those shown in Fig. 3). The swelling results were obtained with benzene at 25° C.; the plastometer hardness figures represent the depth of penetration, in mm./100, of a $^1/_4$ inch diameter ball under a load of 1 kg.

For the rubbers containing different proportions of one material there is a practically linear relationship between swelling and elongation, but the relationship is different for each material. In the case of hardness, the relationship is much more nearly the same for the different types of rubber, so that an approximate linear

correlation between swelling maximum and hardness holds for all the rubbers examined.

A consideration of all the data so far obtained shows that the swelling maximum behaves like a property intermediate between elongation (measured at say 0.75 kg. per sq. mm.) and hardness, but much more closely resembling the latter. This last fact is evidently a consequence of the relative extents of deformation involved in the three tests; thus, the linear deformation produced by swelling in benzene (50–80 per cent) is closer to the 5–20 per cent deformation in the plastometer test than

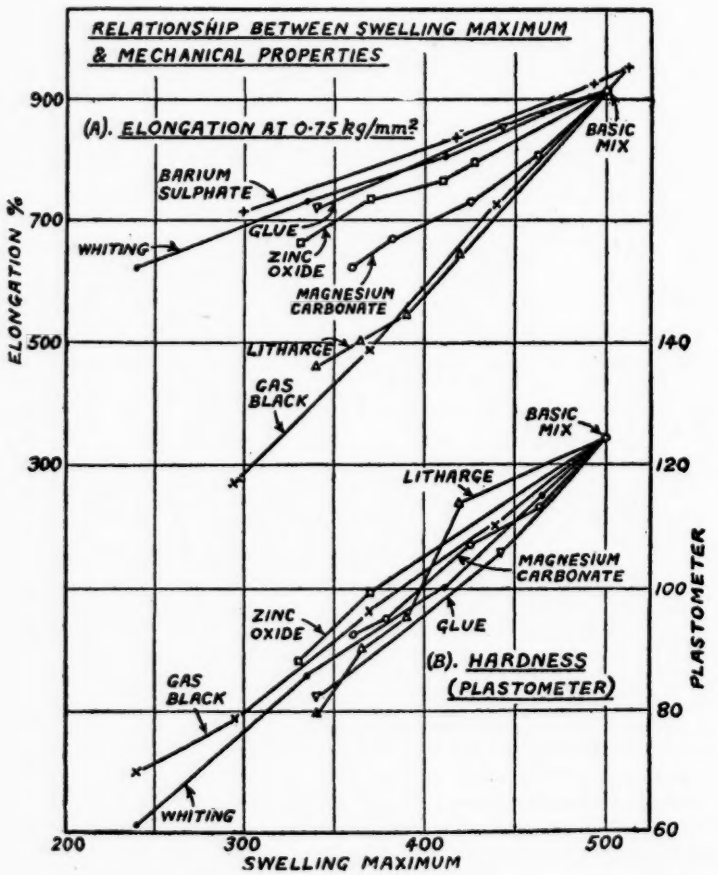



Figure 4

to the 300–900 per cent involved in extension under 0.75 kg. per sq. mm. In short, swelling may be regarded as a form of deformation equivalent to a small linear extension, a view already expressed by Kirchhoff (*loc. cit.*). The logical inference from this is that any rubber which stretches will swell, so that a non-swelling rubber appears to be impossible, a conclusion borne out by tests on several commercial "oil-resisting" rubbers, all of which were found to absorb notable amounts of organic liquids.

The swelling maximum bears no obvious relationship to the other mechanical properties of the rubber, such as tensile strength, resilience or permanent set.

*Increment.*—This seems to be independent of the mechanical properties of the rubber; in particular, no relationship could be found between the increment and the permanent set or slope (type) of the stress-strain curve, such as would be expected if the increment represented a gradual mechanical stretching of the rubber by the internal swelling pressure.

(*c*) *Increment and Aging.*—As the increment appears to be caused by atmospheric oxygen, and as oxidation is the chief cause of the deterioration of vulcanized rubber, it might be expected that the increments of different rubbers would be proportional to the rates of deterioration on aging. Experimental data lend some support to this view, a high increment being often accompanied by poor aging, but there appear to be many exceptions to this rule, and up to the present it has not been found possible to use the increment as a reliable indication of the relative aging properties of different rubbers.

### 7. Practical Applications of Swelling Tests

(*a*) *Oil-Resisting Rubbers.*—The value of swelling tests in this connection is obvious, and it is only necessary to stress the importance of the swelling increment. When rubber is left in contact with a liquid for a very long period, the increment may be responsible for a considerable part of the total swelling, hence it is necessary in testing the rubber to continue the experiment long enough to enable the increment to be determined. In particular, attention must be called to the danger of drawing conclusions regarding the relative swelling capacities of different rubbers or liquids from the swelling after a short period of immersion, since this gives merely the initial rate of absorption, which, as already explained [Section 2, paragraph (*b*)], is no guide to the swelling capacity. In comparisons of rubbers or liquids swelling must be continued at least until the straight part (AB in Fig. 1) of the time-swelling curve has been reached.

(*b*) *Testing Vulcanized Rubbers.*—In connection with rubber testing in general, the swelling maximum, being simply a measure of deformability, can obviously be used in many cases instead of the usual tests such as elongation under constant load, rigidity, or hardness, as for instance in following the changes during progressive vulcanization or those due to addition of compounding ingredients or to aging. The great advantage of the swelling test is that it requires only a very small test-piece, 1 cc. of rubber being a suitable quantity (even 0.1 cc. will suffice), and for this type of work the test-piece need not be of any particular shape; the swelling test is therefore applicable in many cases where the usual mechanical tests cannot be made.

In view of the rapid increase in swelling increment which occurs during natural aging, this property might find application in aging tests on rubber articles from which the usual test-pieces cannot be obtained.

(*c*) *Antioxidants.*—Substances might be tested for antioxidant properties by observing their effect on the increment when added to the swelling liquid (cf. Section 3). From the results so far obtained it appears that substances which lower the increment almost always act as antioxidants, although the magnitude of the reduction in increment does not always indicate correctly the relative antioxidant efficiencies of the substances when used in rubber. Nevertheless, the swelling test should be useful in selecting from a large number of substances those likely to act as antioxidants.

(*d*) *Depolymerization of Vulcanized Rubber; Detection of Deleterious Substances.*—It has not hitherto been possible to examine directly the depolymerization of rubber, *e. g.*, by heat, light, or chemical action, except in the case of raw rubber, where

viscosity tests give the required information. The present investigation shows, however, that the swelling increment furnishes a simple method for following depolymerization changes in vulcanized rubber.

As substances which promote depolymerization increase the increment when added to the swelling liquid, swelling tests could be used to detect injurious constituents in materials which come into contact with rubber or are used in conjunction with it, such as varnishes, tire paints, etc.

In connection with the above applications of the swelling increment, it should be emphasized that these are put forward as suggestions rather than as tried and tested methods, for much further work is still required to obtain a clear understanding of the nature of the increment.

The author wishes to express his thanks to the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish these results, to Mr. B. D. Porritt, for many helpful suggestions during the course of the investigation, to Mr. D. M. Webster, who conducted the earlier experiments with rubber-sulfur, barytes and gas-black mixings, and to Mr. T. R. Dawson, and Mr. T. H. Messenger, for the mechanical testing data and the swelling results for cyclohexane derivatives.

[Reprinted from India Rubber Journal, Vol. 78, No. 10, pages 345-346, September 7, 1929.]

# The Effect of Solvents on the Stress-Strain Curve of Vulcanized Rubber

H. A. Tiltman, B.Sc., and B. D. Porritt, M.Sc., F.I.C., F.I.R.I.

## Introduction

The attention of several investigators has, in the past, been attracted by the changes which occur when rubber—both raw and vulcanized—becomes swollen by a solvent. Up to the present time, however, no serious attempt seems to have been made to study the effect of this swelling on the strength and elastic properties of vulcanized rubber, although it is well known that the material is considerably weakened by the absorption of liquid. In view of the fact that many manufacturing processes include, at some stage, the use of solvents and that certain articles composed essentially of rubber are intended to resist the action of solvents, this omission is somewhat surprising, and it seemed desirable, therefore, to make some preliminary investigations into this effect. Previous researches have been more concerned with the amount of solvent absorbed than in the changes in physical properties resulting from the presence of the solvent. These experiments have usually been carried out by immersing the samples in the solvent, a procedure which is perhaps open to the criticism that soluble constituents such as resins, as well as sulfur in the case of vulcanized rubber, will be extracted by this treatment.

The main object of the present investigation was to determine the effects produced by varying quantities of absorbed solvent on the stress-strain curve of vulcanized rubber, and further to ascertain whether the resultant swelling and contraction produced any permanent effect on the material after the solvent had been allowed to dry off again.

## Experimental

Tests were made with a rubber (specific gravity 1.41) of the following composition:

| | |
|---|---|
| Smoked sheet | 57% |
| Zinc oxide | 39.5% |
| Lime | 0.5% |
| Sulfur | 3.0% |

Tubes 44.6 mm. internal diameter and 5 mm. thick were cured on mandrels in open steam for 3¼ hours at 280 deg. F. (35 lb. steam pressure). The vulcanized tubes were then cut up on the lathe into rings 2 mm. thick, suitable for tensile tests on the Schopper machine.

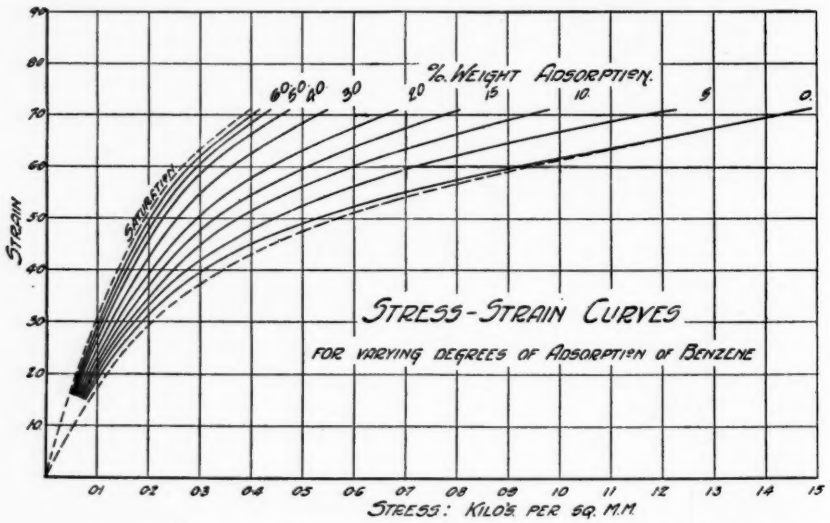
To examine the influence of absorbed solvent, the samples were exposed to the vapor of the solvent; for this purpose the rings were distributed above the surface of a small quantity of benzene contained in a vacuum desiccator, from which the air was subsequently exhausted. All rings were weighed before treatment, and, after varying intervals of exposure, reweighed in a stoppered weighing bottle to determine the absorption and then immediately tested.

No attempt was made to regulate the temperature during the exposure of the rings to solvent vapor or during the subsequent tests, since neither the rate of absorption nor the final saturation value was in question. As the variation in room

temperature was slight, it probably did not materially affect the mechanical testing results. Three rings were used for each test, the results in general proving to be quite uniform.

In all some 20 sets of rings were tested, each representing a different degree of absorption of benzene. In order to present the results in clearer form, the stress-strain curves corresponding to absorption values in round numbers have been obtained by interpolation, and are shown in the accompanying diagram. In these curves the stress is calculated on the original cross-section of the ring (before absorption of benzene), and the strain (elongation) is likewise expressed in terms of the original length of the unswollen ring. It was found that the breaking elongation varied little, if at all, with variation in the degree of absorption, and in the diagram the breaking point has been shown constant at a strain of 7.1 (=710 per cent elongation).

Having examined the immediate effect produced by the absorption of solvent, an attempt was made to determine whether the elastic properties of the rubber had been modified permanently by the swelling to saturation and further partial




or complete evaporation. For this purpose a series of rings was saturated with solvent as before and then allowed to dry, samples being tested at suitable intervals. It was suspected that the accuracy in these tests was not so great as in the absorption series, the reason being that the rapid rate of return to normal conditions resulted in lack of homogeneity throughout the cross-section of the rings. The final set of tests, which represented complete evaporation, should, however, be sufficiently accurate, as the specimens returned to their original weight within about 0.1 per cent, showing the absence of residual solvent. This set of tests is shown in the diagram by a dotted curve, and the change in curvature probably indicates a slight permanent change in elastic properties. The intermediate curves for evaporation have been omitted owing to their doubtful accuracy and because the differences between these and the corresponding absorption curves might not have been observed with more protracted (and therefore uniform) evaporation. It may be safely assumed, however, that the differences between the *up* grade and the corresponding *down* grade curves are at least smaller than that shown at zero absorption.

## Summary and Conclusions

(1) The results indicate that the rigidity of a piece of vulcanized rubber is considerably reduced by the absorption of small amounts of a solvent; thus, at a strain of 6 (=600 per cent elongation) the absorption of 5 per cent by weight (=8 per cent by volume) of benzene lowers the rigidity by 21 per cent.

(2) The greatest effect is produced by the first 20 or 30 per cent (by weight) of absorbed benzene, further absorption having a less marked effect on the stress-strain curve.

(3) The absorption of solvent seems to have very little effect on the breaking elongation, although the tensile strength is considerably lowered. This conclusion, however, is probably no longer true in the case of rubber swollen by immersion in liquid, where the absorption is very much greater than in the present tests.

(4) Absorption of solvent followed by complete drying appears to produce a slight, but technically negligible, permanent effect on the stress-strain curve.

It is evident from these results that when it is necessary to use solvents, either in the process of manufacture or the after-treatment of rubber products, these should be selected as free as possible from high-boiling constituents liable to be permanently retained by the rubber with consequent detriment to its strength.

A conclusion of some theoretical interest is that since all the stresses in the present investigation were calculated on the dimensions of the original dry rubber, the low rigidity of swollen rubber cannot be ascribed simply to the "dilution" of the rubber by the absorbed liquid, but must be due to a loosening of the cohesive forces between the ultimate particles of the material.

In conclusion, the authors wish to take this opportunity of thanking the Board of Management of the Research Association of British Rubber Manufacturers for granting permission to publish these results.

[Translated from Kautschuk, Vol. 5, No. 7, page 150, July, 1929.]

# Color Reactions of Rubber and Gutta-Percha

F. Kirchhof

A previous article of mine entitled "Observations on Color Reactions of Rubber and Gutta-Percha"[1] has led to the question whether intensely colored reaction products which are obtained by fusion of phenols with bromides of hydrocarbons give characteristic absorption spectra.[2] I have carried out a few preliminary experiments on this subject, which appear to confirm my earlier point of view that the cause of the different colorations is to be found in dispersion color reactions.

It is well known that when rubber bromide or gutta-percha bromide is suspended in carbon tetrachloride and is heated with phenol until the carbon tetrachloride is eliminated, a red-violet to blue fusion mixture is obtained, which gives colors of various stabilities depending upon the solvent into which the fusion mixture is dropped. Thus the blue and violet colorations in chloroform are stable for some time, but they change gradually to green and then to brown, with separation of a flocculent precipitate. Yellow-brown reaction products (hydroxyphenylhydrorubber and gutta-percha) are however obtained in the presence of catalysts (iron, aluminum chloride) or by the action of alkalies ($NH_3$, KOH) or by pouring the blue-violet fusion mixtures into ether.

The absorption spectra of a violet and of a yellow-brown solution of approximately the same concentration in chloroform were examined. Both spectra showed almost the same absorption band in the yellow green between 490 and 540$\mu\mu$. Furthermore, the yellow solution showed a more pronounced extinction of the blue and violet part of the spectrum. This behavior of the solutions agrees well with the color-degree of dispersion rule of colloid solutions, according to which the maximum light absorption moves toward the shorter wave lengths with diminishing particle size (yellow solution).

The colloidal nature of colored hydroxyphenylrubber solutions is further substantiated by the following observations. If the solutions mentioned are examined in darkness in a cone of light from an arc lamp, strong Tyndall effects are observed. Blue and violet solutions give intense dark carmine-red effects, yellow solutions pale greenish gray Tyndall light. The colloidal order of magnitude of the particles is evident macroscopically on filtering through a Schleicher-Schüll Weisband filter No. 597. Whereas the blue and yellow solutions pass through almost completely, the particles of the violet and of the green to brown chloroform solutions are almost completely held back on the filter. Accordingly the violet and brown colors originate from the blue and blue-violet solutions by increase in size of the particles. The yellow solutions, which are partially molecular solutions (ammonium or alkali salts of hydroxyphenyl derivatives) are formed from violet solutions by diminution of the particle size.

It is still impossible to say whether besides these dispersoid-chemical causes of the different colors of hydroxyphenylrubber solutions, there are other causes of a valence-chemical nature, *e. g.*, the formation of "carbonium" compounds as suggested by Lecher.[3]

## References

[1] *Kautschuk*, **4**, 190 (1928).
[2] *Gummi-Ztg.*, **42**, 2849 (1928).
[3] According to a communication from Staudinger, the chemistry of the reactions is much more complicated than might be assumed from the investigations of Weber and of H. L. Fisher.

[From Transactions of the Institution of the Rubber Industry, Vol. 5, No. 1, pages 71–83, June, 1929.]

# Heats of Combustion of Rubber, Gutta-Percha, and Balata

T. H. Messenger

Though differing superficially to a considerable degree, rubber, gutta-percha, and balata possess so many properties in common that it is difficult to find an acceptable explanation for the respects in which they differ. The chief suggestions postulate differences in molecular structure or in state of polymerization, and since both might be expected to affect the heat of combustion a study of the value of this property is suggested. Before proceeding to a description of experimental work, the position may be illustrated by reference to the more interesting differences and similarities recorded in the literature.

In connection with specific gravity it has been found that most raw rubbers, which are hard from being stored a long time in the cold, show a sudden change in the value of this property between 30° and 35° C., when slowly warmed. But on cooling, the specific gravity increases but slowly, and only regains its original value after several months' storage in the cold. This phenomenon has been described by Bunschoten (*Mededeelingen van den Rijs-rubberdienst*, 3rd series, 1921) and by Pickles (*India Rubber J.*, **67,** 69 (1924)). It has been reported by Park (*Ind. Eng. Chem.*, **17,** 152 (1925)) that balata behaves similarly, though the time scale is different, being measurable in minutes rather than in weeks, as with rubber.

As regards elastic properties, balata is very tough till stretched about 10 per cent, when it yields and stretches to 200 per cent without any increase in the stretching force. At this elongation it stiffens and ruptures without much increase in the stretch, a high permanent set being retained which is relaxed on warming to 70° C. Though so different at ordinary temperatures, rubber gives similar stress-strain relationships when cooled to −50° C., and stretched, frozen rubber relaxes at about +20° C. (Park, *loc. cit.*). On X-ray examination all three substances give evidence of crystal formation when stretched, though the number of isoprene residues required to build one crystal unit differs.

Striking resemblances are found in the chemical properties. Rubber, gutta-percha, and balata are all hydrocarbons of the formula $(C_5H_8)_n$. They are, therefore, unsaturated. All can be made to take up hydrogen, yielding the compound $(C_5H_{10})_n$, and it has been shown by Staudinger (*Kautschuk*, **1925,** Aug., p. 5; Sept., p. 8) that hydro-rubber, hydro-gutta, and hydro-balata are identical. Alternatively unsaturation may be reduced by internal molecular rearrangement, or "cyclization," and, again, cyclo-gutta and cyclo-balata are identical with cyclo-rubber (Staudinger *loc. cit.;* Geiger, *Gummi-Ztg.*, **40,** 2143 (1926)). Further, Harries (*Natürlichen und Künstlichen Kautschukarten*, **1919,** 122) has shown that by removing hydrogen chloride from its addition compound with gutta-percha a hydrocarbon is obtained which closely resembles that given by similar treatment of the rubber addition product. With gaseous nitric acid all three give the same "nitrosite C" of Harries, having the formula $(C_{10}H_{15}N_3O_7)_2$. The work of Peachey (*J. Soc. Chem. Ind.*, **31,** 1103 (1912); **32,** 179 (1913)) in the case of rubber, and of Dawson and Porritt (*Trans. Inst. Rubber Industry*, **2,** 345 (1927)) in that of balata shows that in the presence of oxygen under suitable conditions both exhibit the S-shaped oxidation-time curve indicative of auto-catalysis. The ozonides of Para rubber and of gutta-percha are identical when pure ozone is employed (Gottlob's *Technology of Rubber*,

1927, 18). On treatment with sulfur the compound $(C_5H_8S)_n$ represents the limit of sulfur addition for all three substances. Pauly (*India Rubber J.*, **75**, 576 (1928)) has found that the color reactions of rubber are given by gutta also, and Scheibe and Pummerer report (*Ber.*, **60**, 2163 (1927)) that in hexahydrotoluene the absorption curve for ultra-violet light of purified gutta-percha is completely identical with that of caoutchouc.

Such, then, are some of the facts awaiting a satisfactory theory for their coordination. The chemical properties of the three compounds indicate that the source of their differences is not located in the fundamental foundation units of the molecule, but in the colloidal state of aggregation of the "macromolecule." But an explanation assuming differences in degree of polymerization is open to objections. Thus, X-ray interference diagrams and temperature stress-strain relationships point to increasing molecular complexity as we proceed from synthetic rubber, through natural rubber to balata, whereas the solution viscosities of rubber and balata point in the opposite direction. This is assuming that increased solution viscosity indicates increased aggregation, an assumption which the observations of Staudinger (*loc. cit.*) on the polymerization of indene seem to justify.

It was in the hope that differences in the heats of combustion might throw light on the situation that the work now to be described was undertaken. Experiments fall into two sections:

(1) Heats of combustion of caoutchouc, gutta-percha, and balata.

(2) Effect of mastication on heat of combustion of rubber.

*Preparation of Materials.*—A sample of unmasticated Para rubber was cut up finely, extracted with ten changes of cold distilled water, dried *in vacuo*, and then extracted for 80 hours with acetone, light being excluded. The extracted rubber was treated with thiophen-free benzene to give a 1 per cent solution, air being excluded by filling the vessel up to the stopper, stirring being induced by introducing pieces of glass and inverting the vessel. By these means some of the rubber was passed into solution, but for complete solution more vigorous stirring was needed. Accordingly the clear supernatant liquid was decanted in the absence of air, and its place taken by air-free carbon dioxide. After vigorous shaking the solution was set aside in the dark to allow insoluble protein and other matter to settle. Completely to eliminate insoluble impurities the solution was finally filtered through closely packed glass wool. This was accomplished without the solution coming into contact with anything except glass, porcelain, and carbon dioxide. Immediately on passing the filter the rubber was precipitated by treatment with excess redistilled absolute alcohol. After keeping a short time under acetone the coagulum was re-

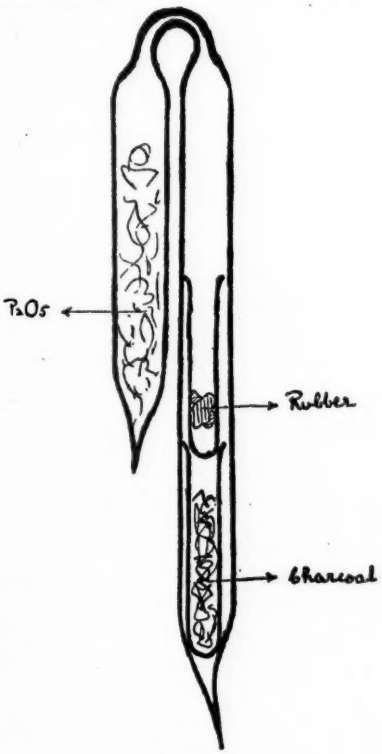



Figure 1

dissolved in chloroform and precipitated by acetone. In subsequent operations no distinction was made between the more soluble portion of the rubber and the remainder.

To remove the last traces of rubber solvent the rubber was placed in a small glass bottle and covered with acetone. The latter was vigorously boiled at room temperature under reduced pressure to remove air, the vessel sealed and allowed to stand several days. This process was repeated till no turbidity was produced on diluting with water. Similar treatment with boiled-out distilled water removed acetone.

The sample was now ready for drying and storing, which was accomplished as follows: About 0.6 g. of material, enough for a single combustion, was removed from the vessel, excess water rapidly blotted off, and the sample placed in a small tube open at one end, which in turn was placed in a specially prepared U-tube, of the form shown in Fig. 1, containing phosphorus pentoxide and animal charcoal. The U-tube was evacuated at the filter pump and filled with nitrogen three times, evacuated once more, and sealed. The tube was hung up in the dark till required.

A similar procedure was adopted for purifying the gutta-percha and the balata, the raw materials possessing, respectively, 15.7 and 37.5 per cent acetone-soluble matter. In both cases warming to 35–40° C. was necessary to effect solution, and ligroin boiling at 60–80° C. was substituted for chloroform in the later stages of the process.

In view of the known difficulty in obtaining rubber hydrocarbon free from oxygen a determination of the carbon and hydrogen content of the final product was made in order to estimate impurities still present. These determinations were made by the usual method of combustion. The average of five analyses on each material gave the following results:

TABLE I

| | % H | % C | % H + % C | No. of H Atoms with 10 C Atoms |
|---|---|---|---|---|
| Rubber | 11.77 | 87.09 | 98.86 | 16.09 |
| Gutta-percha | 11.87 | 86.82 | 98.68 | 16.28 |
| Balata | 11.59 | 85.75 | 97.34 | 16.09 |

The fact that the percentage contents of hydrogen and carbon do not add up to 100 shows that there is still a little oxygen present, and in calculating the heats of combustion an allowance has been made for this factor.

*Heat of Combustion.*—The apparatus used consisted of an oxygen bomb and calorimeter both of standard form. In making a determination the sample was taken from its storage tube, rapidly compressed (when necessary) and weighed in a stoppered weighing bottle. It was placed in a small silica crucible carried by the head of the bomb, and the firing fuse placed in position. This consisted of 5 cm. of fine copper wire strained between two poles connected to the negative and positive terminals of a battery delivering 8–10 volts. Ten cm. of cotton were doubled, tied to the copper wire and placed in contact with the sample in the crucible. The head was then placed in position on the bomb and screwed down tight, oxygen slowly admitted to a pressure of 23 atmospheres, and the bomb placed in the calorimeter, connection having been made to the battery. Temperatures were observed by means of a Beckmann thermometer. When the temperature was steady, or had been changing uniformly for five or six minutes the bomb was fired and temperature readings were taken at one minute intervals until the temperature had been falling regularly for eight or ten minutes.

The readings so obtained were used to calculate the true temperature rise by means of the correction formula given by Regnault and Pfaundler:

$$\text{Correction} = nv + \frac{v^1 - v}{\theta^1 - \theta}\{\Sigma^4\theta + {}^1/_2(\theta_0 + \theta_5) - n\theta\}$$

where $n$ = number of minutes in chief period,
$v$ = rate of fall of temperature per minute during initial period,
$v^1$ = rate of fall of temperature per minute during final period,
$\theta$ and $\theta^1$ = average temperatures during initial and final periods,
$\Sigma^4\theta$ = sum of four readings during chief period, and
${}^1/_2(\theta_1 + \theta_5)$ = mean of firing temperature $\theta_0$ and first temperature of the final period $\theta_5$.

It was found by experiment that no rise in temperature could be detected due to incipient oxidation of the charge in the bomb before firing.

The water equivalent of the calorimeter was determined by means of pure benzoic acid. The following tabulation sets out the heats of combustion found:

TABLE II

| | Heat of Combustion (Cals. per G.) | Average |
|---|---|---|
| Rubber | { 11060, 11010, 10940 / 11110, 10730 } | 10970 |
| Gutta-Percha | { 10890, 10970, 11110 / 11190, 10890, 10880 } | 10990 |
| Balata | { 10840, 11020, 11000 / 11340, 10930, 10890 } | 11000 |

So far as is known, the heat of combustion of rubber has been determined only twice previously. C. O. Weber (*The Chemistry of India Rubber*, 5th ed., **1919,** p. 107), using very carefully purified selected Para rubber, obtained a value of 10669 cals. per g., a result somewhat lower than that found in the present work. Kirchhof and Matulke (*Ber.*, **57,** 1266 (1924)), using pale crepe previously extracted with acetone for 12 hours and dried *in vacuo* to constant weight, found the heat of combustion to be 10700 cals. per g. As regards the heats of combustion of gutta and balata, no reference has been found to this property having ever been determined, and the results herewith reported have therefore a special interest. It will be noticed that within experimental error, the heats of combustion of the three substances are the same (to within 0.3 per cent), and so far from it being possible to draw conclusions as to differences in structure based on different heats of combustion, these results but add one more example to those already noted of the striking similarity in chemical properties of rubber, gutta-percha, and balata. Thus no deductions can be drawn as to differences in degree of polymerization. As regards the existence of isomerism some structural isomers have different heats of combustion, while others have been found to be almost identical in this respect. It may, however, be mentioned that stereo- and position-isomers nearly always have the same heat of combustion, and the suggestion that rubber, gutta-percha, and balata are stereoisomers has already been put forward by Miedel (*Gummi-Ztg.*, **41,** 2369 (1927)).

*Effect of Disaggregation on the Heat of Combustion of Rubber.*—Before raw rubber has been subjected to the mechanical working and high temperatures which accompany the usual methods of its manufacture into useful articles it possesses considerable tensile strength, toughness, and "nerve," and gives extremely viscous solutions. Rubber in this condition is considered to be highly polymerized or to possess a high degree of aggregation. By the expenditure of energy either in the form of heat or by mechanical working, the rubber can be progressively plasticized

till it becomes soft and tacky and gives comparatively fluid solutions. Such rubber is said to be depolymerized or disaggregated.

These terms are not synonymous, and rubber technologists have been accused of using them loosely (Fisher, *Ind. Eng. Chem.*, **16,** 627 (1924); **18,** 414 (1926)). Polymerization is a chemical term denoting the combination of simple unsaturated molecules with one another by means of main valencies, the reverse process being depolymerization. Aggregation and disaggregation, on the other hand, are physical processes, or at the most physicochemical, and are concerned with the much larger particles associated with the colloidal state. Although rubber can be truly depolymerized, its physical breaking down is better referred to as disaggregation.

It is admitted generally that milling causes disaggregation, but opinion is divided as to whether depolymerization, properly so called, takes place. Dinsmore (*Ind. Eng. Chem.*, **18,** 1149 (1926)) holds that it does not, and quotes the work of Kelly and Kurtz, who found that the rate of reaction of rubber with sulfur chloride was unaffected by mastication. But Harries (*Natürlichen und Künstlichen Kautschukarten*, **1919,** p. 50), on the other hand, has shown that milled rubber is more easily oxidized by potassium permanganate and more easily hydrogenated (Harries, *Ber.*, **56,** 1048 (1923); Fisher and Gray, *Ind. Eng. Chem.*, **18,** 414 (1926)) than is unmilled rubber. Greinert and Behre (*Kautschuk*, **1926,** March, p. 63), and also Boiry (*Le Caout.*, **21,** 12257 (1924)) found that in the hot vulcanization of rubber solutions by sulfur the time to gelation was increased by the use of milled rubber. If, as is usually supposed, vulcanization leads to increased polymerization, it would seem that a larger quantity of polymerization work has to be done on the milled sample than on the unmilled to lead to gel-formation, and that milling has therefore produced depolymerization. Boiry found also that subjecting the rubber to previous heat treatment gave a similar result, presumably for the same reason. Bary (*Rev. Gén. Caout.*, **1926,** March, p. 5; April, p. 3) has the hypothesis that for each temperature there is a state of equilibrium in the degree of aggregation, a lowering of temperature leading to increased aggregation, and vice versa.

In view of the above observations, and since both heat and milling involve the expenditure of energy on the rubber, it might be expected that milled rubber would possess a greater heat of combustion than the same rubber unmilled. Indirect evidence against this is found in the observation of Williams and Beaver (*Ind. Eng. Chem.*, **15,** 255 (1923)) and of Bysow (*J. Russ. Phys.-Chem. Soc.*, **53,** 79 (1921)) that in the case of soft rubber (low sulfur content) the heat of combustion was unchanged by vulcanization. Against this may be set the work of Kirchhof and Matulke (*loc. cit.*) which appeared while that about to be described was projected. These authors determined the heat of combustion of raw rubber, and of the same rubber after it had been acted on by sulfuric acid in an invert solvent. Polymerization occurred with increase in specific gravity, but the molecule now contained sulfur dioxide. Figures are quoted which support the contention that polymerization is accompanied by an increase in specific gravity and a decrease in heat of combustion.

*Experimental.*—Two methods of disaggregation were employed: (1) Mechanical mastication; (2) exposure to sunlight.

A piece of pale crepe was divided into three portions. One was left untreated. The second was treated mechanically as follows:

(1) The rollers of the mill were thoroughly cleaned and the rubber was masticated, using a tight nip and cold rolls. From time to time portions were cut from the main body of the mass as milling proceeded. The process was continued until

the rubber was reduced to a sticky pasty mass. Each sample removed from the mill was stored for some months in a stoppered tube, after which a measure of the state of aggregation was obtained by determining the solution viscosity in benzene, and the heat of combustion of the range of samples carried out. The viscosity changes brought about by progressive mastication are set out graphically in Fig. 2.

(2) Sunlight has both an aggregating and disaggregating effect on rubber, the latter predominating (Asano, *India Rubber J.*, **70,** 307, 347, 389 (1925)). If rubber so exposed is treated with a solvent the disaggregated portion passes into solution

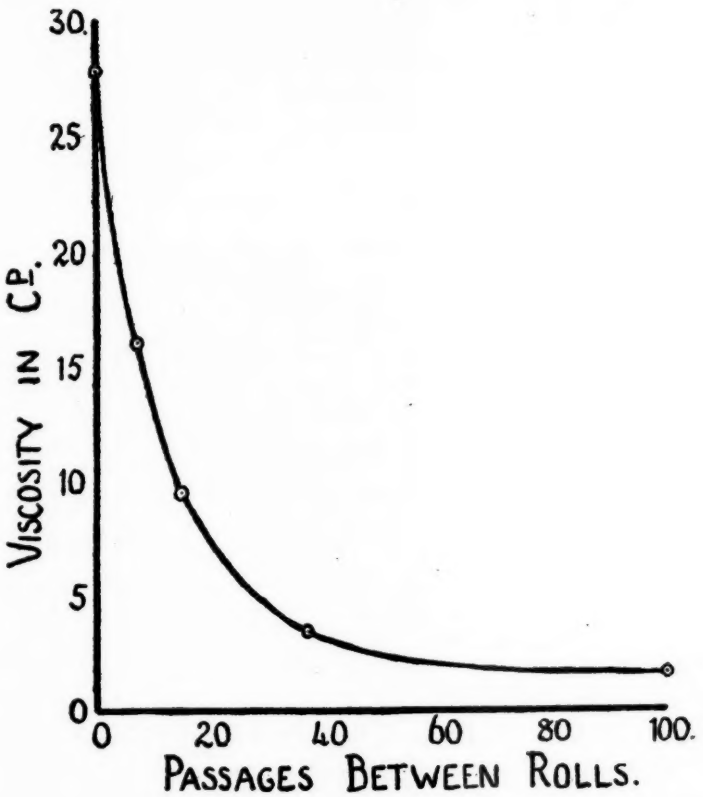



**Figure 2—Disaggregation of Rubber by Milling**

without appreciably affecting the viscosity, while the remainder merely swells, and does not dissolve. Therefore the third portion was treated thus:

The rubber was finely shredded and accurately weighed out into portions of 0.6000 g. (a suitable quantity for a heat of combustion determination). Each portion was placed in a glass tube and the air removed at the filter pump (10–12 mm. pressure). Nitrogen was admitted. The whole process was repeated twice, after which the pressure was again reduced, and the tubes were sealed. Oxygen was removed because in sunlight oxygen combines with rubber. The tubes were then exposed out of doors (0 to 29 days during June and July).

Heats of combustion were obtained for the range of samples, and are set out below.

TABLE III

MASTICATED RUBBER

| Millings | Viscosity | Heat of Combustion | Cals. per G. Average |
|---|---|---|---|
| 0 | 27.9 | 10650, 10580<br>10740, 10720 | 10670 |
| 7 | 16.1 | 10670, 10590 | 10630 |
| 15 | 9.6 | 10640, 10630 | 10640 |
| 37 | 3.4 | 10660, 10650 | 10660 |
| 100 | 1.5 | 10630, 10610 | 10620 |

RUBBER EXPOSED TO SUNLIGHT

| Days' Exposure | Heat of Combustion | Cals. per G. Average |
|---|---|---|
| 3 | 10640 | 10640 |
| 9 | 10640 | 10640 |
| 29 | 10610, 10630 | 10620 |

The viscosity figures in the above table are centipoises at 25° C. of a 1 per cent by weight solution in benzene.

Although the viscosity figures show that disaggregation has been very severe, viscosity changing from 27.9 to 1.5 centipoises, yet no measurable change has taken place in the heat of combustion. Neither does exposure to sunlight affect this property to a greater extent, in spite of the fact that great changes in solubility had occurred. From these results it is concluded that internal *molecular* changes (depolymerization) do not occur during milling or exposure to sunlight, and that changes observed are due to physical changes in the state of aggregation.

## APPENDIX

### DISCUSSION OF CARBON-HYDROGEN RATIO IN RUBBER, GUTTA-PERCHA, AND BALATA

Although the empirical formula $C_5H_8$ is ascribed to caoutchouc, the published analyses often deviate from this very considerably. Thus, concerning gutta-percha, Caspari (*J. Soc. Chem. Ind.*, **24**, 1274 (1905)) reports that after five precipitations and drying in hydrogen, the material still contains 1 per cent of oxygen, though "recrystallization" from ligroin was stated to give a pure product.

C. O. Weber (*loc. cit.*, p. 6) publishes results of analyses of purified rubber by Faraday, Ure, Williams, Berzelius, Adriani, and Gladstone and Hibbert, in which the hydrogen content is reported as ranging from 10.0–12.8 per cent, and the carbon from 87.2–90.0 per cent. Gladstone and Hibbert (*J. Chem. Soc.*, **1888**, 60), indeed, consider the complete removal of oxygen to be impossible. Further, Weber tabulates analyses of rubbers, all purified by extraction with acetone, followed by solution in a large volume of chloroform, and fractional precipitation by absolute alcohol, in which the oxygen content ranges from 0.61–2.53 per cent. By very careful fractionation of a 0.1 per cent chloroform solution, Weber obtained a sample containing only 0.23 per cent oxygen.

D. Spence (*Kolloid Z.*, **4**, 70 (1909)) reports two analyses which showed 2.92 per cent and 2.95 per cent oxygen.

Impressed by these and similar figures, Kirchhof (*Kolloid-chem. Beihefte*, **16**, 47 (1922)) went into the question very fully, and published his findings in a long paper, the conclusion reached being that the empirical formula should be written $C_{10}H_{17}$.

It would appear, however, from the recent work of Pummerer and Burkard (*Ber.*, **55**, 3458 (1922)), who worked with very carefully purified rubber, that the

$C_5H_8$ ratio has been substantiated, and Kirchhof (*Kautschuk*, Sept., 1925, p. 10) has retracted his suggestion that it should be $C_{10}H_{17}$.

Similarly the analyses of gutta-percha show considerable variation. The following figures were noted in a search of the literature, and are arranged chronologically:

TABLE IV

| Observer | % H. | % C. | Sum | H. Atoms to 10 C. Atoms |
|---|---|---|---|---|
| Soubeiran[1] "Pure" | 11.3 | 83.5 | 94.8 | 16.07 |
| Maclagan[2] | 12.15 | 86.36 | 98.51 | 16.74 |
| Oudemans[2] "Pure gutta" | 11.79 | 87.64 | 99.43 | 16.16 |
| | 11.77 | 88.10 | 99.87 | 15.91 |
| | 12.01 | 88.29 | 100.30 | 16.20 |
| Hofmann.[2] Precipitated from ether by alcohol | 12.50 | 88.10 | 100.60 | 16.91 |
| Adriani.[2] "Very pure" | 11.94 | 87.91 | 99.85 | 16.18 |
| Miller[2] | 12.04 | 87.22 | 99.26 | 16.45 |
| Oesterle[2] | 11.34 | 88.56 | 99.90 | 15.29 |
| | 12.18 | 87.69 | 99.87 | 16.48 |
| | 11.51 | 88.31 | 99.82 | 15.49 |
| Fendler[2] | 10.93 | 86.93 | 97.86 | 14.97 |
| | 10.98 | 87.07 | 98.05 | 15.02 |
| | 11.21 | 87.29 | 98.50 | 15.30 |
| Ramsay, Chick, and Collingridge.[3] "Very pure." Precipitated from chloroform by alcohol | 11.75 | 88.31 | 100.66 | 15.83 |
| Weber (*loc. cit.* p. 11). "Pure." Acetone-extracted, precipitated from chloroform by alcohol | 11.78 | 88.01 | 99.79 | 15.93 |
| Müller.[4] Recrystallized from ether and dried in hydrogen | 11.64 | 88.26 | 99.88 | 15.69 |
| | 11.91 | 87.78 | 99.69 | 16.15 |
| | 12.15 | 88.21 | 100.36 | 16.54 |

The average of the figures in the last column gives the empirical formula $C_{10}H_{15.96}$, thus confirming the usually accepted $C_{10}H_{16}$ formula. This ratio is also confirmed by the following authors, but figures are not published: Baumhauer, Montpelier (*J. Soc. Chem. Ind.*, **16**, 925 (1897)), Caspari (*loc. cit.*), and Potts (*The Chemistry of the Rubber Industry*, **1920**, 5th Ed., p. 68).

Data relative to the composition of balata are less numerous and more contradictory, as the following table illustrates:

TABLE V

| Observer | % H. | % C. | Sum | H. Atoms to 10 C. Atoms |
|---|---|---|---|---|
| Sperlich[5] | 11.37 | 88.49 | 99.86 | 15.31 |
| Weber (*loc. cit.*). Acetone-extracted, dissolved in chloroform and precipitated with alcohol | 11.69 | 86.34 | 98.03 | 16.18 |
| Schereschewski.[6] Dissolved in toluene precipitated by alcohol, dried in carbon dioxide or in hydrogen at 100–110° C. (Mean or four) | 13.93 | 87.39 | 101.32 | 18.94 |
| Crystallized from chloroform-alcohol-ether mixture and dried in carbon dioxide. (Mean of five) | 13.20 | 87.25 | 100.45 | 18.02 |

The figures obtained by Schereschewski appear very abnormal. The method employed by him of drying in an atmosphere of carbon dioxide was tried by Müller when working with gutta-percha, but he discarded it in favor of drying in hydrogen.

[1] See Seeligmann, Torrilhon, and Falconnet, *Indiarubber and Gutta-Percha*, 1910, p. 374.

[2] See Müller, *Beiträge zur Chemie der Gutta-Percha and des Kautschuks*, 1905, pp. 10–15.

[3] Ramsay, Chick, and Collingridge, *J. Soc. Chem. Ind.*, **21**, 1367 (1902).

[4] Müller, *loc. cit.*, p. 37.

[5] Sperlich. See Schereschewski, *Über Balata und Chicle*, **1906**, 45.

[6] Schereschewski, *loc. cit.*, pp. 79–81.

Caspari (*loc. cit.*) confirms the formula of $C_{10}H_{16}$ for balata without quoting figures. The results obtained during the present research given an empirical formula of $C_{10}H_{16\cdot09}$, and also point very definitely in the same direction.

The author desires to express his thanks to the Board of Management of the Research Association for permission to carry out most of the work in the Association's Laboratories, and to Professor W. A. Bone and Mr. F. Brinsley for facilities to carry out the heat of combustion determinations in the Fuel Laboratories of the Imperial College of Science and Technology.

[Translated from Kautschuk, Vol. 5, No. 9, pages 200–202, September, 1929.]

# The Berginization of Raw Rubber

**H. I. Waterman, R. H. Dewald, and A. J. Tulleners**

As a raw material for the experiments, a sample of raw rubber, *viz.*, first latex crepe, was used. This was obtained from the Reichskautschukprüfungsanstalt in Delft, where analysis showed the particular sample of crepe contained 93 to 94 per cent rubber hydrocarbon, with the remaining 6 to 7 per cent composed of 2 to 3 per cent acetone extract, 2 to 3 per cent proteins (calculated as protein with factor 6.25) and finally moisture and ash.

When dry distilled in the ordinary way, this crepe yielded up to 450° C. about 95 per cent of a yellow oil which was highly unsaturated. The bromine addition number (according to the McIlhiney method) of the distilled benzine (b. p. up to 220° C.) was, with a 3-minute contact period in carbon tetrachloride in darkness, higher than 120. The benzine obtained from the berginization of the raw rubber was far different from this.

The experiments were carried out in an agitated autoclave. Five iron balls served as a means of stirring. In each experiment 150 g. of crepe were rolled around the pyrometer tube in the autoclave. Each time before an experiment, the autoclave was evacuated and was charged with hydrogen at 110 kg. per sq. cm. pressure. Two experiments, $D_6$ and $D_7$, were carried out. For comparison 2 similar experiments, $D_3$ and $D_4$, were made in which hydrogen under pressure was not used, in this case the heating being carried out under the pressure of the gases formed by the thermal decomposition. The conditions used in the $D_3$ and $D_4$ experiments were otherwise identical with those of the $D_6$ and $D_7$ experiments. The heating was carried on so that 450° C. was reached as rapidly as possible, at which point the system was maintained for 15 minutes. At the end of this period of heating, the autoclave was cooled rapidly by compressed air. After cooling the gases were drawn off through a previously evacuated spiral receptacle cooled with a carbon dioxide–acetone mixture. Whatever was not condensed in this way was collected in a gas-measuring receiver. After the pressure in the autoclave had fallen to one atmosphere, the autoclave valve was closed, the cold mixture was removed from the spiral, as a result of which the liquid condensed within the spiral evaporated in part.

The gases obtained by this evaporation were mixed with those collected earlier in the experiment. In the calculations 0.9 and 0.2 liter were allowed for the gases remaining behind in the autoclave and in the spiral receptacle, respectively. The liquid which remained in the spiral was added to that poured out of the autoclave. This liquid was filtered to free it of deposited carbon. The carbon was washed with low boiling benzine and dried to constant weight.

A tabular summary of the quantities and the properties of the products which were formed are shown below.

| | $D_3$ | $D_4$ | $D_6$ | $D_7$ |
|---|---|---|---|---|
| No. of g. of crepe treated | 150 | 150 | 150 | 150 |
| No. of g. of hydrogen added | 0 | 0 | 0 | 0 |
| No. of l. of gas at end (0° C., 760 mm.) | 11.0 | 9.6 | 81.7 | 81.9 |
| No. of g. of gas at end | 10.3 | 9.0 | 15.0 | 15.0 |
| No. of g. of liquid | 126.7 | 127.9 | 140.5 | 139.5 |
| No. of g. of carbon | 2.3 | 2.6 | 0.0 | 0.0 |
| | 139.3 | 139.5 | 155.5 | 154.5 |

| | | | | |
|---|---|---|---|---|
| No. of g. of loss | 10.7 | 10.5 | 2.2 | 3.2 |
| % benzine (b. p. below 220°) on latex | 39.7 | 40.0 | 43.6 | 43.9 |
| % kerosene (b. p. 220–300°) on latex | 21.1 | 20.2 | 24.7 | 22.2 |
| Br. no. of benzine (McIlhiney method) | 33 | 34 | 40 | 39 |
| Br. no. of kerosene (McIlhiney method) | 13 | 12 | ... | 13 |
| $n_D^{20}$ of benzine | 1.4611 | 1.4591 | 1.4500 | 1.4507 |
| $n_D^{20}$ of kerosene | 1.5195 | 1.5191 | 1.5029 | 1.5019 |
| Aniline point of benzine | +3.6° | +4.1° | +20.1° | +21.0° |
| Aniline point of kerosene | +4.3° | +2.6° | ... | +23.5° |
| No. of g. (net) of hydrogen consumed | ... | ... | 1.2 | 1.1 |
| No. of g. of hydrogen evolved | 0.18 | 0.17 | ... | ... |

The properties of the benzine and the kerosene obtained in the berginization experiments differ from those of the products obtained in the cracking experiments. The index of refraction is lower and the aniline point considerably higher than with the products from cracking. In spite of the fact that in the berginization more than 1 gram of hydrogen was consumed, the bromine number does not point to a higher saturation. Yet the benzine and the kerosene obtained in the berginization are more stable, at least the corresponding products from cracking turn brown rapidly on standing in the air. There are other differences, *e. g.*, the Engler residues from the $D_6$ and $D_7$ experiments were the thinner liquids, and in contrast to the density of the residues from cracking the density of the residues from the berginization was less than 1, while finally no carbon was formed in the berginization. Acknowledgment is made of the collaboration of D. J. van Wijk in the experimental work.

[Translated from Kautschuk, Vol. 5, No. 7, pages 151–152, July, 1929.]

# Structural Differences in Masticated and Unmasticated Raw Rubber Mixtures and Vulcanizates, and Their Significance from a Practical Point of View

**E. A. Hauser**

**In collaboration with M. Hünemörder**

The use of latex in certain branches of the rubber industry is even today looked upon with a great deal of skepticism in technical circles. This point of view rests not so much on ignorance of actual progress in this field as on the still prevalent idea that a mixture of latex and fillers can never give a useful product and one comparable in quality with a raw rubber mixture. This belief is based on the fact that latex is a decidedly heterogeneous system, since the rubber in latex is distributed throughout in the form of individual particles. In spite, however, of this current belief there is now satisfactory evidence to show that products made from latex mixtures without mastication of the rubber are superior in almost all their physical properties to products made from raw rubber in the conventional way. This superiority is in evidence particularly in the higher tensile strength and elasticity and in the incomparably better resistance to tearing.

The experiments to be described, which are based in part on work already published elsewhere and on still unpublished investigations of Miss Hünemörder and the author, will serve to make clear the theoretical basis on which these facts rest and will furthermore indicate a few points which in our opinion are worthy of special consideration in the preparation of latex mixtures.

A microscopic examination of a thin slice of smoked sheet will reveal the fact that, aside from impurities, there is optically no structure. If however, such a thin section is thoroughly digested in water for several hours and is then examined as before, the original structure of the closely packed latex particles is distinctly in evidence. This change depends upon the fact that the layer of resin and protein which is strongly adsorbed on the particles swells to such an extent that the index of refraction of this adsorbed layer is enough different from that of the rubber particle to make the interface visible.

If now smoked sheet is masticated and from time to time thin sections are sliced from it and digested in water, it is found that the aforementioned structure disappears with increasing mastication and that a corresponding almost homogeneous optical effect is obtained. The cause of this is naturally the progressive destruction of the structure of the latex particles. A completely masticated sheet, such for example as is used in the manufacture of "patent" rubber products, shows practically no structure of latex particles. Vulcanization has little effect on this phenomenon, in as much as with well regulated vulcanization only isolated sulfur crystals are observable, and these are orientated in the mass in the typical crystal formation which has already been described frequently.

If such a sheet is cut or notched, even a slight stretching will cause the cut to

travel across the whole sheet. With sheets which have been calendered the orientation of the "crystallized phase" still persists, so that tearing perpendicular to the direction of calendering is rendered somewhat more difficult. If, however, a sheet is prepared from latex by evaporation or by suitable coagulation, details of which will not be described here, and this sheet is properly vulcanized, then it is found that the material offers considerable resistance to further tearing when a notched piece is stretched. The cause of this depends upon the character of the microstructure, which resists further tearing. So much for articles of pure rubber. It might only be pointed out further that many times latex films show low resistance to tear, in which case the cause may be a two-fold one. Either the material is not wholly dry so that the individual particles are separated by a non-adherent resin-protein or a water layer through which the tear proceeds easily, or vulcanization has been unsatisfactory and a more or less profound thermochemical mastication has occurred. As is known, depolymerization of the hydrocarbon takes place at the beginning of vulcanization, and under certain conditions this may lead to a homogeneous fusion of the disperse hydrocarbon phase. In both cases this phenomenon may with certain assumptions be proved microscopically.

The second part of the subject concerns loaded mixtures. Here with raw rubber we must distinguish between mixtures containing fillers which merely dilute and mixtures containing fillers which exert on the rubber a so-called "reënforcing" effect. There has been much theorizing about the causes of these differing effects, but in our opinion there is no generally satisfactory theory even today to account for these differences. On the other hand the distinction can be very beautifully demonstrated by simple empirical experiments. Fillers like barytes and chalk, which can be regarded only as diluents, show under the microscope, when the rubber mixture is stretched, a clean-cut loosening or separation from the surrounding rubber matrix. Distinct vacuoles are formed in which the filler particles lie more or less free. In these cases tearing goes on at the interface of the surface of the filler and the rubber without marked resistance. Reënforcing fillers show a high power of adhesion, or in technical language they are easily wetted. Here the interfacial affinity opposes the tearing and this affinity is considerably greater than the cohesion of the rubber matrix itself, so that here tearing can take place only in the rubber matrix among the particles. Since these fillers are in general very finely divided, the tearing must follow a very tortuous path, as a result of which rubber mixtures containing gas black have their well-known high resistance to tearing.

In the case of loaded latex mixtures, the effect depends less upon the wetting, since the individual latex particles behave quite differently from the masticated rubber matrix. Here adsorption forces play a part, for the fillers are bound more or less weakly to the surface of the individual latex particles by these forces. Accordingly besides the adsorptive power there is the magnitude of the purely geometrical surface area to be taken into account, for this latter is necessary to the intimate union of the particles. If a latex mixture is overloaded with filler, so that the total surface of the individual latex particles is occupied by the filler particles, then it is comprehensible that tearing can proceed comparatively easily by the mere rupture of the filler medium. In the practical preparation of latex mixtures, attention must always be paid to the fact that in most cases the proportions of filler are not the same as the proportions which give the best results in raw rubber mixtures. In latex mixtures this phenomenon depends to a greater extent upon the degree of dispersion of the fillers than with raw rubber mixtures, so that here too in our opinion of the technology of latex (which in spite of the adverse comments appearing now and then in technical circles seems well justified) an intensive study of the improvement of dispersion of fillers is urgently needed.

It is hoped that this discussion will succeed, as mentioned in the beginning, in refuting the prevalent but erroneous idea that latex mixtures are of poorer quality than raw rubber mixtures. At the same time it is hoped that the discussion has made clear the most important points which on purely theoretical grounds must be taken into consideration in the preparation of latex mixtures.

Finally it is hoped that by calling attention to the importance of a study of the dispersion of fillers, further evidence is available to show that latex chemistry is no longer to be regarded as merely a favorite pursuit for scientific amateurs, but has become a source of enrichment of rubber chemistry in general and therefore has made itself indispensable.

**Discussion**

R. PUMMERER.—Can differences in the degree of dispersion of gas blacks be detected by the solubility of the rubber in the mixtures? There are said to be rubber-gas black mixtures which give up hardly any rubber to solvents. But as far as I know, there are no definite data in the literature, and only the heats of swelling have been measured by Hock.

H. KROEPELIN.—Stamberger has carried out diffusion experiments with and without admixed gas black and has found that a rubber-gas black mixture does not diffuse freely but that the gas black and the rubber advance through the solvent as a homogeneous swollen mass. I believe, that in diffusion measurements of rubber, one does not measure the diffusion of free rubber micelles but rather the entrance of the solvents in a distending gel. In any case it has been proved that in a diffusion experiment with rubber in benzene after a certain time the same quantity of rubber is present in all four strata; at the same time this was not the case in a corresponding experiment in which the micelles must have been either deprived of swelling power or further subdivided, for the viscosity was considerably lower in this last experiment.

E. A. HAUSER.—There is a difference between the diffusion of rubber alone and of rubber with gas black, as may be seen from the experiment described below. On the one hand a mixture of rubber and active gas black is dissolved in benzene and on the other hand rubber alone is dissolved in benzene and the active black is added to the solution. When each is centrifuged, the gas black separates only from the second solution.

[Translated from Le Caoutchouc & la Gutta-Percha, Vol. 26, No. 308, pages 14722-14730, October 15, 1929.]

# An Attempt at a Rational Classification of the Principal Accelerators of Vulcanization

## II. A Study of the Time Required for Vulcanization Giving the Maxima Physical Properties at Different Temperatures

R. Thiollet and G. Martin

We have attempted to classify the principal accelerators of vulcanization according to their chief characteristics which are the following:

(1) Time necessary for the fixation of mixtures at different temperatures.

(2) Times required at different temperatures to obtain vulcanization giving the maxima physical properties.

(3) Aging.

The first of these 3 items has been treated in *Caoutchouc et Gutta-Percha* (April, *1929*) and we have shown how accelerators can be classified by their "precocity" of action; that is to say, by the rapidity with which they "fix" mixtures at different temperatures.

The mixture being fixed, vulcanization continues and the physical quality of the rubber improves. It thus reaches a maximum, then diminishes upon too prolonged heating.

In this second study we have attempted to determine the following points:

(1) At a given temperature, how long a period of vulcanization is required to impart to the mixtures their maxima physical properties?

(2) Within the range of temperatures, which temperature gives the optima physical properties?

The experiments were carried out on the following type mixing:

| | |
|---|---|
| Pale crepe | 100 |
| Zinc oxide | 5 |
| Palm oil | 1 |
| Stearic acid | 0.5 |
| Accelerator | ... |
| Sulfur | ... |

The following table gives the proportions of sulfur and of accelerators used:

| No. | Accelerator | % Sulfur on Rubber | % Accelerator on Rubber |
|---|---|---|---|
| 1 | Zinc isopropylxanthate | 2 | 2 |
| 2 | Zinc methylphenyldithiocarbamate | 1.8 | 0.7 |
| 3 | Tetramethylthiuramdisulfide | 1.8 | 0.4 |
| 4 | Mercaptobenzothiazole | 2.5 | 0.7 |
| 5 | Diphenylguanidine | 3 | 0.7 |
| 6 | Di-*o*-tolylguanidine | 3 | 0.6 |
| 7 | Phenyltolylxylylguanidine | 3 | 0.6 |
| 8 | Ethylidene-aniline | 3.5 | 1 |
| 9 | *p*-Nitrosodimethylaniline | 3.5 | 1 |
| 10 | Thiocarbanilide | 5 | 2.5 |
| 11 | Anhydroformaldehyde-*p*-toluidine | 3.5 | 1 |
| 12 | Triphenylguanidine | 3.5 | 1 |
| 13 | Anhydroformaldehyde-aniline | 4 | 2 |

All the mixtures were made up from the same lot of crude rubber and the experiments were carried out under analogous conditions in practically equal periods of time.

*Vulcanization Tests.*—With each of the mixtures and at a definite temperature a series of cures under pressure were made. The times of vulcanization were:

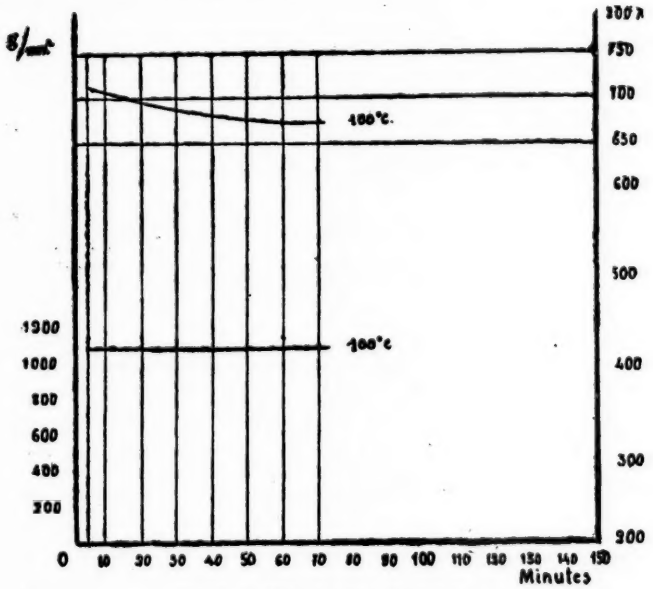
10 minutes—10 × 2 min.....10 × *n* min.

With very active accelerators cures were made every five minutes. This series of cures was repeated at the following temperatures, expressed in steam pressure:

3.5; 3.0; 2.5; 1.5; 1.0; 0.5 kg.; no pressure

With certain accelerators which act only at relatively high temperatures, the series at low temperatures were not carried out.

From each of the vulcanized mixtures thus obtained, three test rings of carefully determined dimensions were cut, the elongation and tensile strength being measured. The mean of the three results was used.



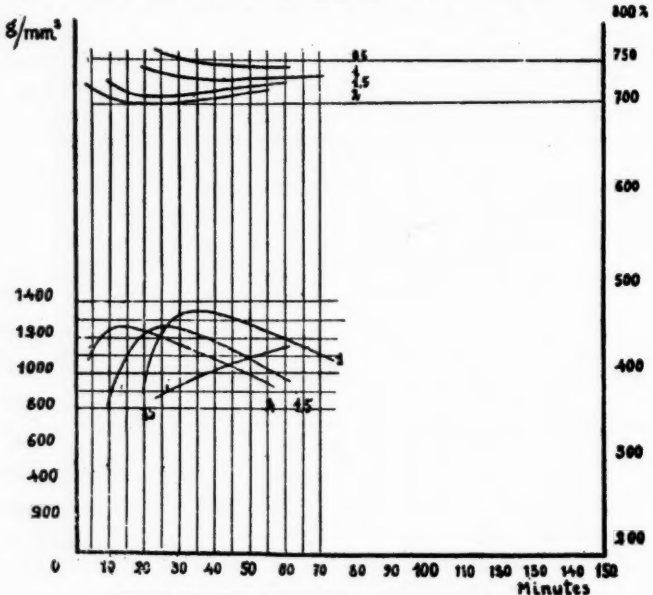

**Graph I—Zinc Isopropylxanthate**

*Representative Curves.*—By using rectangular coördinates with the abscissae representing the times of vulcanization and the ordinates the tensile strengths, we have established a series of isothermic curves showing how the tensile strength varies with increase in time of vulcanization. Analogous curves have been determined for the per cent elongation at rupture.

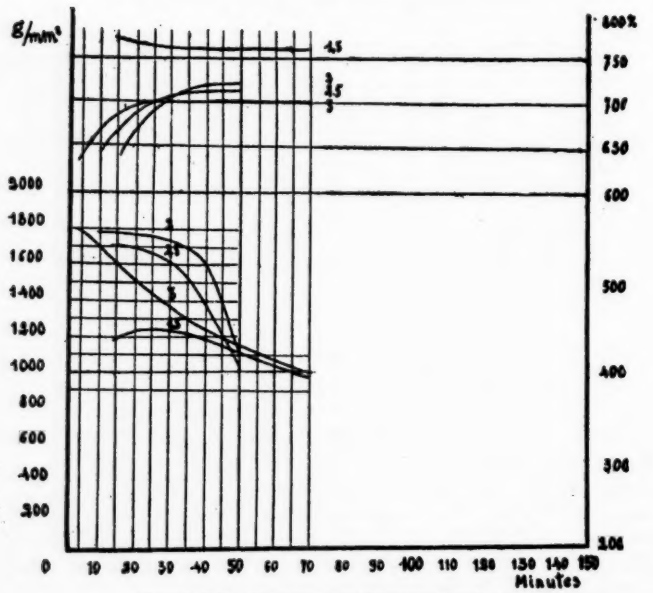
Each of the curves representing the variations in resistance to stress passes through a minimum or tends to become parallel to the abscissa. In general, at the point where the curve of stresses no longer has a clean-cut rise, the elongation tends to become constant. For mixtures having a low proportion of sulfur (for example those vulcanized with zinc methylphenyldithiocarbamate) the elongation, after having diminished, again increases while the stress at rupture diminishes, that is, the mixture softens. A devulcanization of some sort has been brought about.

In order to make our classification, we paid especial attention to an examination

of the curves of variation of the tension at rupture as a function of the time of vulcanization. In all the accompanying graphs the time of vulcanization in min-



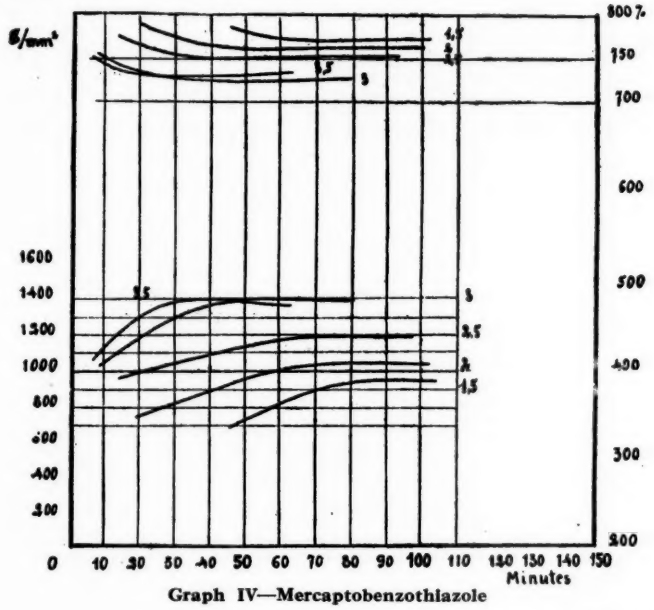

Graph II—Zinc Methylphenyldithiocarbamate



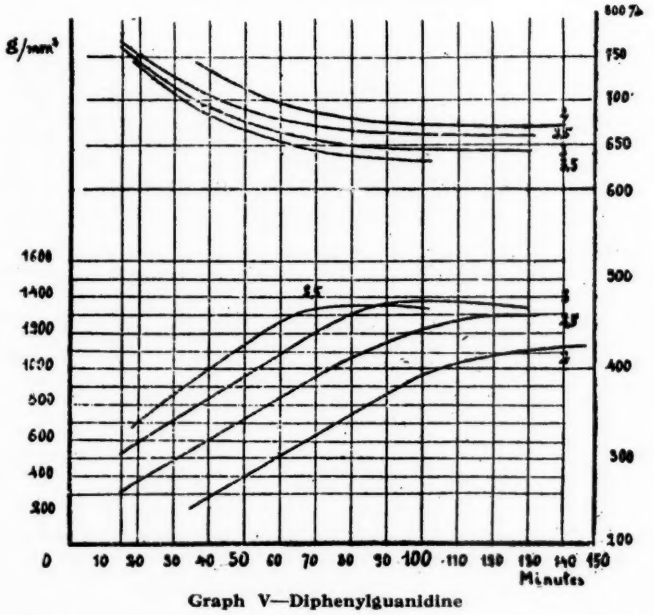

Graph III—Tetramethylthiuramdisulfide

utes is shown on the X axis. The group of curves located nearest the abscissa corresponds to the stresses at rupture in grams per sq. mm., indicated on the left

ordinate. The group of curves farthest from the abscissa corresponds to the per cent elongations at rupture, indicated on the right ordinate.



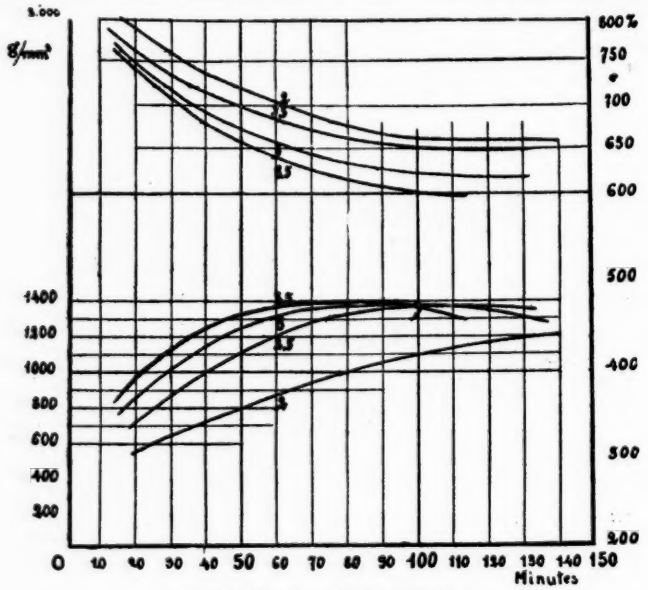

Graph IV—Mercaptobenzothiazole



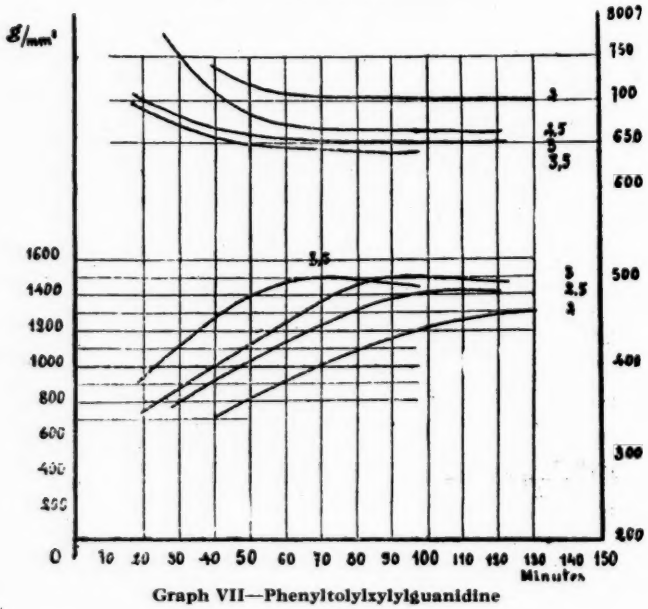

Graph V—Diphenylguanidine

The number for each curve indicates the steam pressure at which the corresponding cure was made.

*Method of Classification.*—In the series of curves relating to a particular accelerator, we chose that which corresponded to the optima physical properties, that



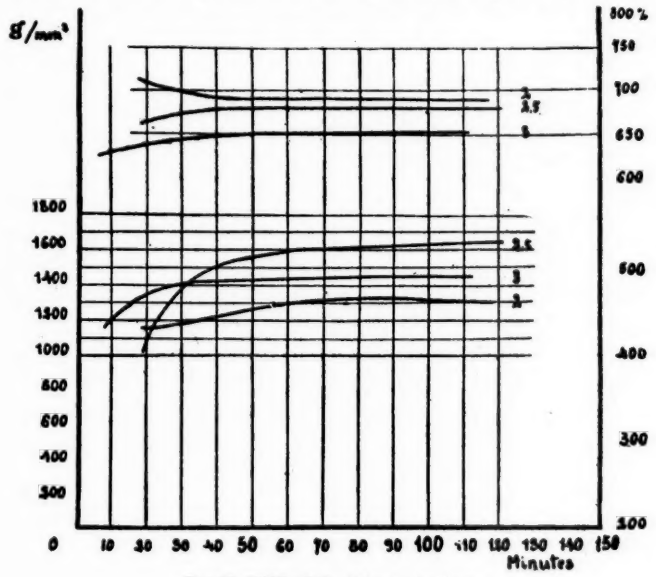

**Graph VI—Di-*o*-tolylguanidine**



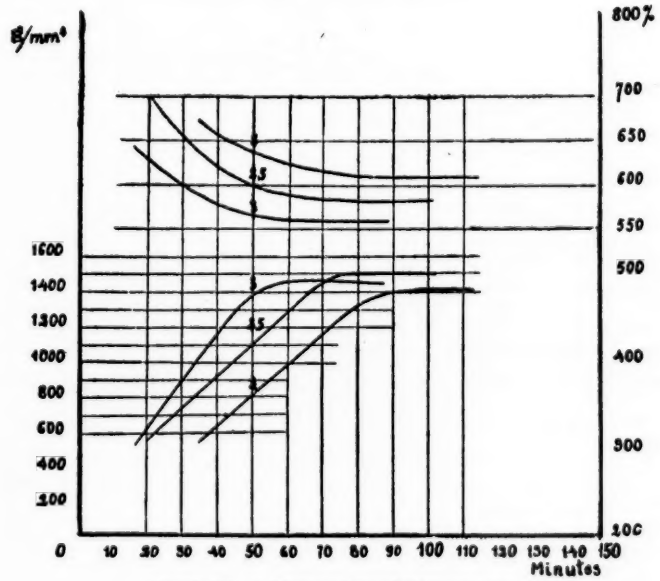

**Graph VII—Phenyltolylxylylguanidine**

is, the one which gave the maximum tensile break. A temperature corresponding to this curve is called the characteristic temperature of the substance in question.

This temperature, having been determined for each of the accelerators, the latter could be classified according to the time required to impart the optima physical




Graph VIII—Ethylidene-Aniline



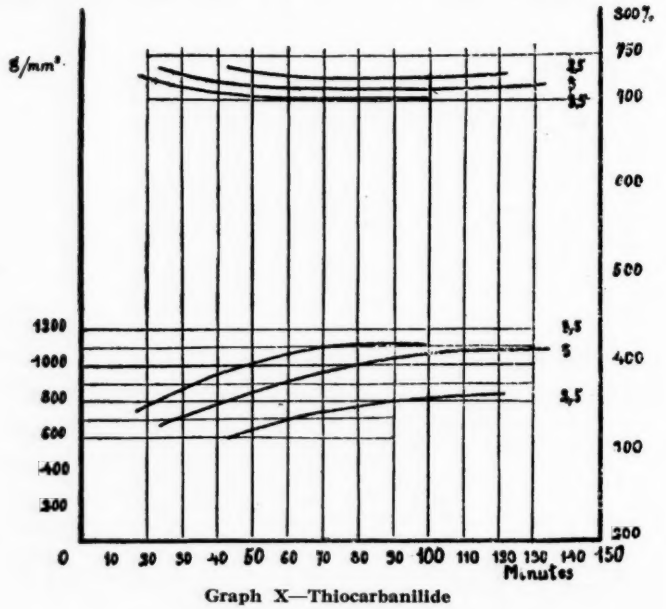

Graph IX—*p*-Nitrosodimethylguanidine

properties to the mixtures when cured at the characteristic temperatures. We have summarized the results in a double column table—giving for each accelerator

on the one hand the characteristic temperatures $T$ and on the other the time of heating $t$ required to impart to the mixtures the maxima physical properties when vulcanized at this characteristic temperature.

*Example.*—Ethylidene-aniline is shown by a point located at the intersection of a vertical line corresponding to the temp. of 2.5 kg. (steam pressure) and of a horizontal line corresponding to 50 minutes, because with this product, it is necessary to vulcanize at 2.5 kg. (characteristic temperature) for 50 minutes to obtain a mixture having the optima physical properties.

By examining this synoptic chart the most favorable conditions of time and temperature for each accelerator can be determined. The charts so made can be divided by horizontal lines, each interval corresponding to 20 minutes, and in this way accelerators are grouped according to their rapidity of action at a characteristic temperature. Each accelerator can in this way be given a coefficient ranging from 1 to 6 which will represent its rapidity of action at a characteristic temperature.




**Graph X—Thiocarbanilide**

### Effect of the Simultaneous Use of Two Accelerators

A study of several examples of the simultaneous use of two accelerators mentioned in the attached graph led to some very interesting observations:

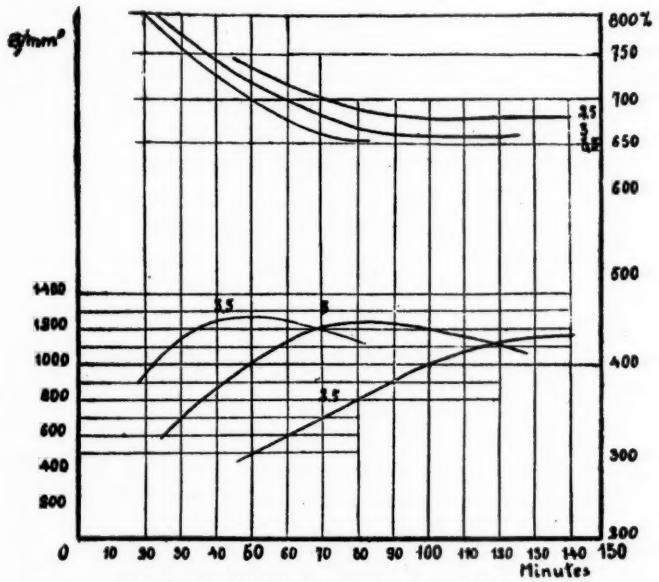
| Accelerator | % Sulfur on Rubber | % Accelerator on Rubber |
|---|---|---|
| Mercaptobenzothiazole | | 0.3 |
| Ethylidene-aniline | 2.5 | 0.45 |
| Mercaptobenzothiazole | | 0.3 |
| Diphenylguanidine | 2.5 | 0.4 |
| Zinc methylphenyldithiocarbamate | | 0.7 |
| Anhydroformaldehyde-aniline | 1.8 | 1 |

The graphs show that mercaptobenzothiazole in combination with ethylidene-aniline or diphenylguanidine behaves like a very active accelerator, possessing a

high vulcanizing power for products of this class. Further it is of great interest to note that these mixtures of accelerators impart to the cured rubber a high tensile strength with a very satisfactory elongation.

*Example.*—A mixture containing 0.3% mercaptobenzothiazole and 0.45% ethylidene-aniline vulcanized for 20 minutes at 133° C. (2 kg.) has, at rupture, a tensile strength of 2100 g. and an elongation of 680 per cent.

A mixture of mercaptobenzothiazole and diphenylguanidine gives similar properties, but the characteristic temperature is lower than in the preceding instance (125° C.).



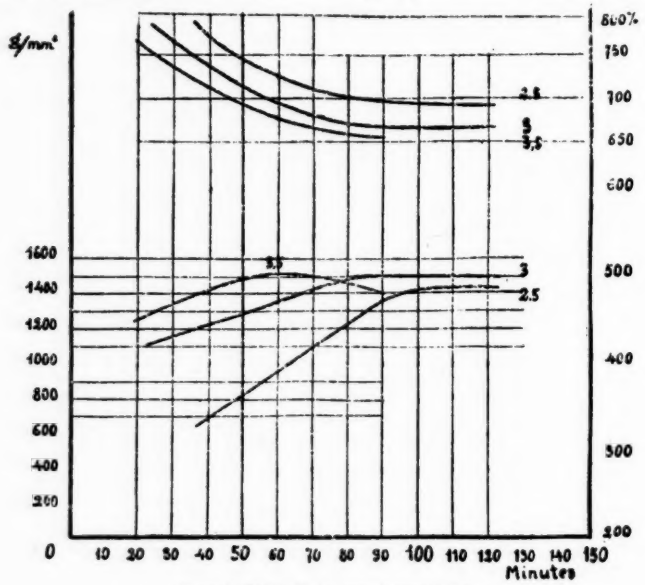

**Graph XI—Anhydroformaldehyde-*p*-toluidine**

## Control of the Action of Rapid Accelerators by the Simultaneous Use of Another Accelerator

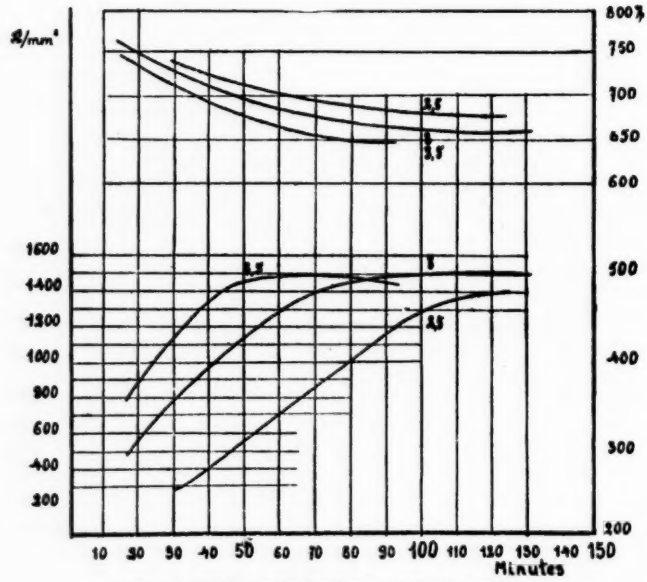
In the first part of this study we have already established the fact that it is possible to retard the "precocity" of action of rapid accelerators by the joint use of another accelerator. We have already studied the particular action in the case of a mixture vulcanized with zinc methylphenyldithiocarbamate and we have shown that the "precocity" of this accelerator is retarded by the joint use of anhydroformaldehyde-aniline.

We have continued this study from the point of view of the rapidity of vulcanization and we have ascertained that the rapidity of action of zinc methylphenyldithiocarbamate at different temperatures is the same with the addition of anhydroformaldehyde-aniline. The presence of the latter product has no other influence, therefore, on the course of vulcanization than to retard the rapidity of fixation of the mixture, the maxima physical properties being obtained with the same time of heating. It must be mentioned however that the presence of anhydroformaldehyde-aniline improves perceptibly the physical properties of the vulcanized mixture. In short, rapid accelerators can be made easier to handle without decreasing their activity.

*Remarks on the Xanthates.*—As with the other accelerators, we have not carried out a series of vulcanizations with zinc isopropylxanthate which we selected as



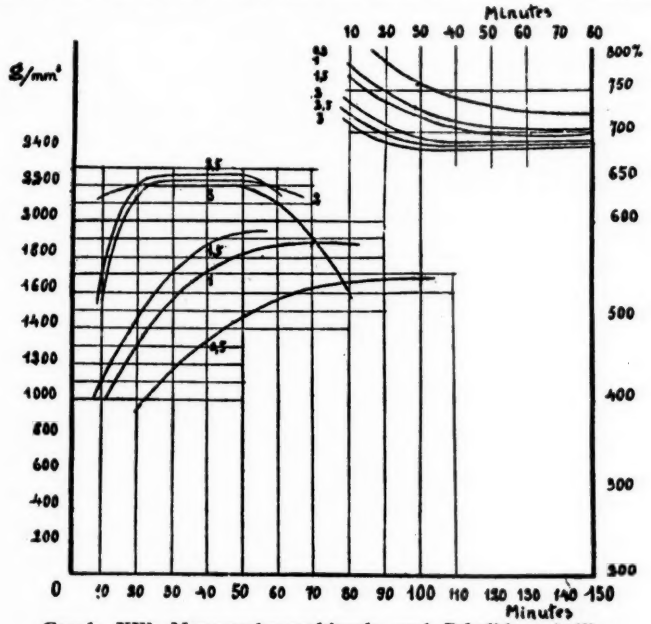

**Graph XII—Triphenylguanidine**



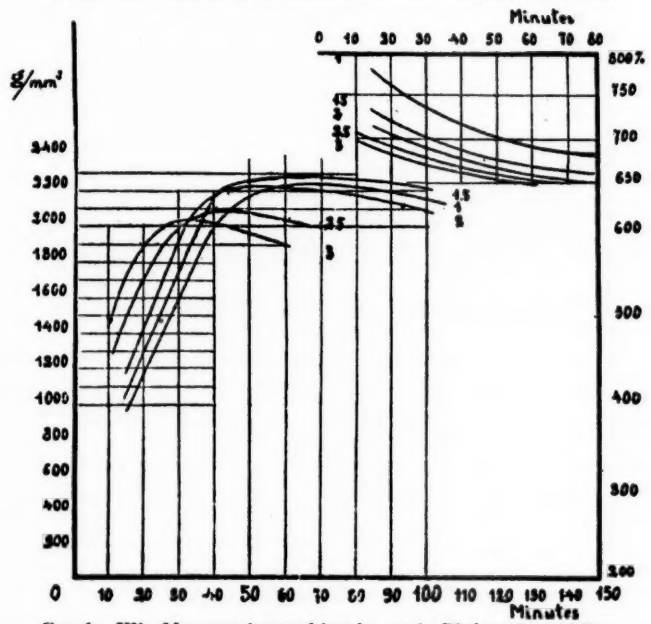

**Graph XIII—Anhydroformaldehyde-Aniline**

typical of this class of accelerators. These substances are in fact most often used under special conditions, for example, in self-curing solutions. We have merely

carried out a series of vulcanizations at 100° C., so as to show its behavior at a relatively high temperature (it begins to act at ordinary temperature). We show on the graph, that in a very short time the mixture reaches its maxima physical



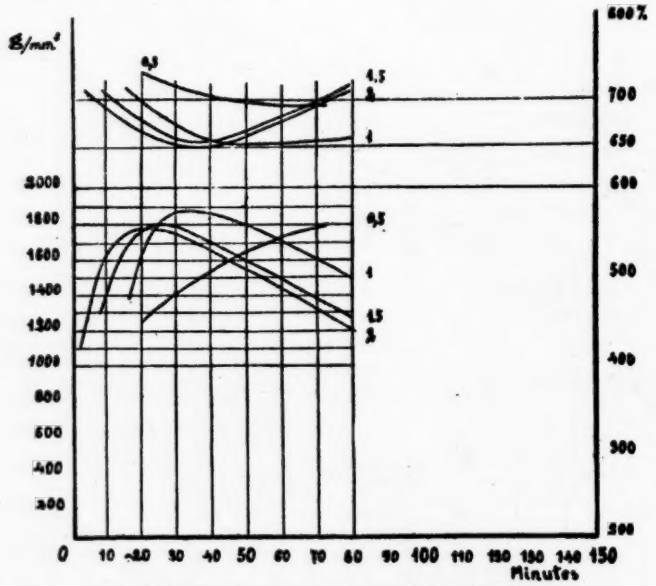

Graph XIV—Mercaptobenzothiazole and Ethylidene-Aniline




Graph XV—Mercaptobenzothiazole and Diphenylguanidine

properties and that these remain constant when the cure is continued, proving that the accelerator is destroyed by the heat and that consequently its action ceases after a very short time. The state of cure to which a mixture can be brought can therefore be varied only by the proportion of accelerator used.

*Plateau of Vulcanization.*—The idea of a "plateau of vulcanization" is very important for the rubber industry. A long plateau reduces the dangers of over-cure and permits the uniform cure of large masses of rubber. Making allowance for certain substances which decompose during the course of vulcanization, the dangers of over-cure are encountered especially in the use of very rapid accelerators for which an extra few minutes of cure may constitute a relatively great error in the time of cure. It is therefore particularly interesting to note, from this new point of view, that mixtures of mercaptobenzothiazole with ethylidene-aniline and diphenylguanidine behave like rapid accelerators, giving a remarkable "plateau of vulcanization" as shown in graphs XIV and XV. On the contrary, tetramethylthiuramdisulfide, which is extremely active, has a very much reduced "plateau of vulcanization." (Graph III)



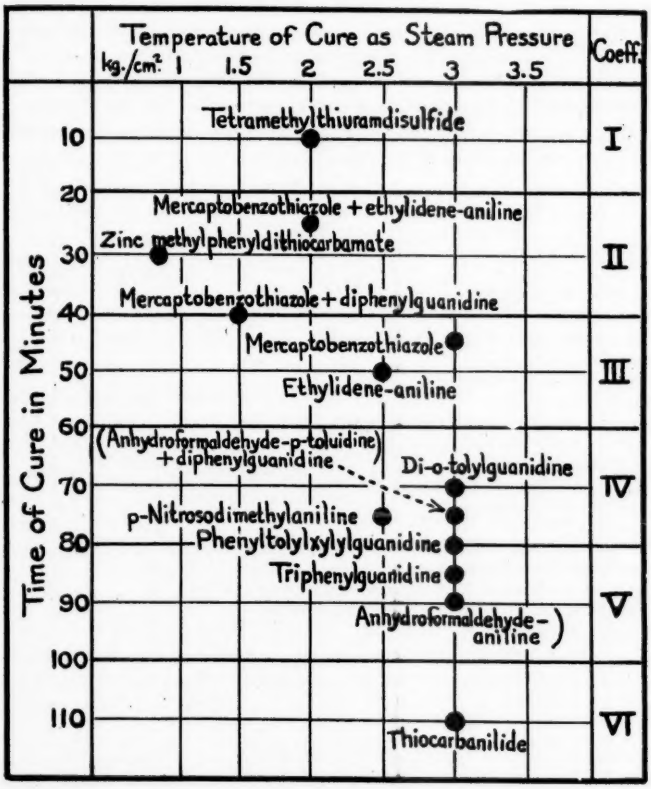

**Graph XVI—Zinc Methylphenyldithiocarbamate**

One should also observe the very broad plateaus of mercaptobenzothiazole and of ethylidene-aniline (Graphs IV and VIII), which are rather active accelerators, (coefficient 3) but which lend themselves to the cure of thick articles due to their long plateau of vulcanization.

In practice, as a result of the influence of the charges in the mixtures and also because of the better preservation of the vulcanized articles (a subject which we shall study in future experiments) noticeably lower temperatures of vulcanization are actually used than those which correspond, in our curves, to the maxima physical properties. Nevertheless, examination of the curves will give useful indications (1) of the rapidity of action of the accelerators at different temperatures and (2) of the temperature of vulcanization which must be adopted for each so as to obtain

the best results. It should be mentioned, however, that accelerators can be used at other temperatures than their characteristic temperature, but knowledge of this characteristic temperature can be of assistance in the choice which must be made every time an accelerator is to be used for a particular process. Thus zinc methylphenyldithiocarbamate which fixes mixtures at a sufficiently low temperature and causes a progressive vulcanization proceeding at its best at 120° C., is very suitable for vulcanizing rubberized fabrics in hot air, a process which is usually carried out at this temperature.

SYNOPTIC CHART




Thiocarbanilide, a precocious accelerator, is also often used for this type of vulcanization which requires a quite rapid fixation of the mixture. Most of the time either an organic accelerator (diphenylguanidine) or a more active mineral accelerator (litharge) is used with it to complete its action and to permit it to come more quickly to complete vulcanization, once fixation has been brought about.

In treating large masses of rubber two methods are possible to bring about a homogeneous vulcanization of the entire article.

(1) The use of an accelerator which is not active at low temperatures and the resulting accomplishment of a rise of long duration so that vulcanization will commence throughout the mass only when the latter has been completely brought to the characteristic temperature. The accelerators which are best adapted to these long cures are anhydroformaldehyde-aniline and anhydro-formaldehyde-*p*-toluidine.

(2) A shortening of the rise, and the use of an accelerator which is more precocious but which has a very extended plateau of vulcanization, permitting a prolonged heating of the outer portions without changing their properties. Ethylidene-aniline fulfils these requirements very well.

*Conclusions.*—The methodical examination of the physical processes of the phenomena of vulcanization shows that in speaking of the activity of an accelerator the following three factors should be considered:

(1) Precocity.

(2) Temperature of normal action (characteristic temperature).

(3) Rate of vulcanization at different temperatures and especially at the characteristic temperature.

The following table shows the properties of the accelerators which have been studied in the particular mixture used. As for precocity, unit 1 indicates the greatest precocity while 6 represents the weakest.

With regard to the rapidity of action at the characteristic temperature, unit 1 indicates the greatest rapidity and 6 the slowest.

| | Accelerator | Coefficient of Precocity | Coefficient of Rapidity of Action at Characteristic Temp. | Characteristic Temperature (Steam Pressure) |
|---|---|---|---|---|
| 1 | Zinc methylphenyldithiocarbamate | 2 | 2 | 1 kg. |
| 2 | Thiocarbanilide | 3 | 6 | 3 |
| 3 | Ethylidene-aniline | 3 | 3 | 2.5 |
| 4 | Mercaptobenzothiazole | 4 | 3 | 3 |
| 5 | Tetramethylthiuramdisulfide | 4 | 1 | 2 |
| 6 | Phenyltolylguanidine | 5 | 4 | 3 |
| 7 | Diphenylguanidine | 5 | 4 | 3 |
| 8 | *p*-Nitrosodimethylaniline | 5 | 4 | 2.5 |
| 9 | Di-*o*-tolylguanidine | 5 | 4 | 3 |
| 10 | Anhydroformaldehyde-*p*-toluidine | 6 | 4 | 3 |
| 11 | Anhydroformaldehyde-aniline | 6 | 5 | 3 |
| 12 | Triphenylguanidine | 6 | 5 | 3 |
| 13 | Zinc methylphenyldithiocarbamate and anhydroformaldehyde-aniline | 3 | 2 | 1 |
| 14 | Mercaptobenzothiazole and diphenylguanidine | 3 | 2 | 1.5 |
| 15 | Mercaptobenzothiazole and ethylidene-aniline | 3 | 2 | 2 |
| 16 | Zinc isopropylxanthate | 1 | ... | ... |

[Translated from Gazzetta Chimica Italiana, Vol. 59, No. 8, pages 544–548, August, 1929.]

# Condensation Products of Aminophenols with Aldehydes

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The chemical literature on the condensation products of aminophenols with aldehydes is somewhat meagre and the only condensation products which are known are those from *p*-aminophenol and some aromatic aldehydes. There was accordingly a certain amount of interest in carrying out experiments on the condensation products of other aminophenols with aldehydes. This was particularly true of 2,4-diaminophenol, since in this case derivatives of a diamino compound too unstable to be isolated in a pure state should add to our general knowledge of diamino compounds. The interest in these compounds is also due to the fact that some of them may easily find useful applications in the rubber industry.

The condensation products which are described below were obtained by the reaction of aldehydes in aqueous solution, or if insoluble in aqueous suspension, with the calculated quantity of aminophenol, or even better by the reaction of aldehydes with the hydrochloride of the amine or diaminophenol in the presence of sodium acetate. The hydrochloride of the condensation product is thus precipitated, and after the addition of sodium carbonate or sodium bicarbonate, the condensation product itself separates. With aldehydes insoluble in water, the operation is carried on preferably with the addition of acetic acid, and the separation of the bases made with excess soda. Acetic acid is then added until the base soluble in excess of alkali separates. The products described below have not been known, with the exception of methylene-*p*-aminophenol, which in doubtful form has been prepared from *p*-aminophenol and formaldehyde in dilute alkaline solution.

## Derivatives of *p*-Aminophenol

*Methylene-p-aminophenol* $p\text{-}HOC_6H_4N{:}CH_2$.—This has already been prepared from *p*-aminophenol and a dilute alkaline solution of formaldehyde. It is an infusible brown powder insoluble in ordinary solvents and is probably a polymer.

*Ethylene-p-aminophenol* $p\text{-}HOC_6H_4N{:}CHCH_3$.—This is similar to the preceding compound.

*Furfurylidene-p-aminophenol* $p\text{-}HOC_6H_4N{:}CHC_4H_3O$.—Crystallized from alcohol, it is yellow and fuses at 176.5° C. It gives a *hydrochloride* which is orange.

*o-Nitrobenzylidene-p-aminophenol* $p\text{-}HOC_6H_4N{:}CHC_6H_4NO_2$.—Crystallized from benzene, it is yellow and fuses at 154° C.

*Terephthalidene-p-aminophenol*.—Crystallized from alcohol, it is yellow and fuses at 256° C.

## Derivatives of *o*-Aminophenol

*Methylene-o-aminophenol* $o\text{-}HOC_6H_4N{:}CH_2$.—Like the corresponding product from *p*-aminophenol, this is a brown powder and is probably a polymer.

*Ethylidene-o-aminophenol* $o\text{-}HOC_6H_4N{:}CHCH_3$.—This is similar to the preceding compound.

*Furfurylidene-o-aminophenol* $o\text{-}HOC_6H_4N{:}CHC_4H_3O$.—This is a brown powder somewhat soluble in ordinary solvents.

*o-Nitrobenzylidene-o-aminophenol* $o\text{-}HOC_6H_4N{:}CHC_6H_4NO_2$.—Crystallized from benzene, this forms large scales of an intense yellow color, fusing at 104° C.

*Terephthalidene-o-aminophenol.*—Crystallized from alcohol, this is yellow and fuses at 213° C.

### Derivatives of *m*-Aminophenol

These derivatives are quite similar to the corresponding ones from *o*-aminophenol.

### Other Derivatives

*Dimethylene-2,4-diaminophenol* $HOC_6H_3(N{:}CH_2)_2$.—This is an orange color and is insoluble in ordinary solvents. It is probably a polymer.

*Diethylidene-2,4-diaminophenol* $HOC_6H_3(N{:}CHCH_3)_2$.—This is brown, but otherwise is similar to the preceding substance.

*Di-isovaleralidene-2,4-diaminophenol* $HOC_6H_3[N{:}CHCH_2CH(CH_3)_2]_2$.—Crystallized from benzene, this a yellow powder. Its *hydrochloride* is red, and crystallized from water fuses at 126° C.

*Difurfurylidene-2,4-diaminophenol* $HOC_6H_3(N{:}C_5H_4O)_2$.—This is a pitch somewhat soluble in ordinary solvents.

*Dibenzylidene-2,4-diaminophenol* $HOC_6H_3(N{:}CHC_6H_5)_2$.—Crystallized from alcohol, this is yellow and fuses at 106°.

*Disalicylidene-2,4-diaminophenol* $HOC_6H_3(N{:}CHC_6H_4OH)_2$.—Crystallized from benzene, this is red and fuses at 170° C.

*Dicinnamylidene-2,4-diaminophenol.*—The *hydrochloride* was prepared. It separates readily from water.

*Divanyllidene-2,4-diaminophenol.*—Crystallized from benzene this is red. Its *hydrochloride* is yellow.

*Terephthalidene-2,4-diaminophenol.*—This is yellow, is infusible, and is insoluble in ordinary solvents.

### Summary

In the present note condensation products of the simpler aminophenols with aliphatic and aromatic aldehydes are described The condensation products with aldehydes and 2,4-diaminophenol are of particular interest because the latter is so unstable that so far as known it has not been directly isolated.

Some of these condensation products may well have useful applications in the rubber industry.

[From Transactions of the Institution of the Rubber Industry, Vol. 5, No. 1, pages 31-43, June, 1929.]

# The Aging of Cotton Contained in Rubber Goods

**Guy Barr**

The paper will not deal with the behavior of such textiles as tire fabrics and cords in service and any general remarks made should be interpreted as applying, in the first place, to balloon fabrics, though some of them will not need the restriction. The subject of the permeability of balloon fabrics to hydrogen or to air will not receive attention, as the aging of the cotton has no direct connection with the variations of permeability which occur on exposure.

*Early Observations on the Weathering of Balloon Fabrics.*—Rubbered cotton had been used on the Continent by the end of last century in the construction of balloons, but the authorities here had put their faith in goldbeaters' skin when building small spherical balloons, so that when attention was directed toward dirigibles, this country had to make up considerable lee-way in the study of rubbered fabrics suitable for such purposes. The manufacturing difficulties which are involved in obtaining satisfactory gas-tightness with a limited weight of rubber proved only a temporary trouble. The chief defect of early balloon fabrics was the relatively rapid rate of increase of permeability, but it was recognized that deterioration of the cotton was of vital importance; if an airship did not continue to hold gas well it was liable to fall gradually, but if the cotton had become weakened a burst was almost certain to involve loss of life.

Under the auspices of the Advisory Committee for Aeronautics, experiments on the weathering of balloon fabrics were commenced at the National Physical Laboratory in 1910. Although the results of these experiments are not now of much more than historical interest, a point in connection with the tensile strength was rather unexpected. Some doubled fabrics were exposed on the roof for successive intervals of about a month and their tensile strengths measured from time to time. From some preliminary tests it was anticipated that the strength might fall, in the absence of any actinic protection, to about one-half of its original value after an exposure of four autumnal months, and it was remarkable to find that after one month's exposure the material was actually stronger, as judged by a tensile test, than when new. This result was confirmed in several cases for fabrics protected by dyes, etc., when exposed for about a month during the summer. The increase in strength amounted to nearly 15 per cent for one parallel doubled yellow dyed balloon fabric. For a similar but uncolored fabric, protected during exposure from the action of rain, the following results were obtained:

TABLE I

| Exposure, "days" | New | 24 | 48 | 72 | 96 | 120 |
|---|---|---|---|---|---|---|
| Tensile strength, kg. per m | 1050 | 1030 | 1145 | 1025 | 928 | 850 |
| Permeability liters at 15° C. per sq. m. per day | 9.3 | 1.8 | 1.1 | 34 | Large | |

The acetone extract of the rubber after 48 days had increased from 5 per cent to 54 per cent.

The increase in strength is in reality neither very surprising nor genuine. It is due to a sort of sizing effect of the rubber on the cotton, the perished rubber locking the fibers together and preventing the yarns from slipping and twisting during the

tensile test. Judged by a tearing test, the fabric would have been found much weaker than when new; similar results are now well-known in the case of aeroplane wing fabric as the effect of doping with cellulose acetate or nitrate solution.

Since ultra-violet light was suspected to be active in causing deterioration of the rubber, it was suggested many years ago (originally by Victor Henri) that the outer ply of cotton in a doubled fabric should be colored yellow so as to act to some extent as a screen to prevent actinic light from reaching the rubber. This practice was fairly general before 1910, lead chromate impregnation being used with cold vulcanization and aniline dyes for hot vulcanization. In the above series of exposures it was found that such protection was not only effective in retarding the perishing of the rubber, as judged by permeability tests, but was also useful in preserving the strength of the cotton.

About 1914 some samples of fabric were tested which had been exposed to the light in Berbera, and these were found to have suffered rapid deterioration in spite of the presence of a yellow dye on the outer ply of cotton. In the tensile test it was observed that this outer ply gave way at a load some 20–30 lbs. per inch before the test-piece broke, and behaved as though it had been tendered by acid. The writer had recently been examining the effect of light on some experimental samples of ebonite, exposed in moist air; the inferior samples yielded visible sulfuric acid on the surface, which was collected and titrated. The tendered balloon fabric was similarly tested, and after soaking in water sulfuric acid was found to be present to the extent of nearly half a gram per square meter of surface. According to some data which have become available since that time, this acidity is of about the same order as that which is retained on unproofed fabric which has been soaked in 0.05*N* $H_2SO_4$ solution and dried between sheets of filter paper; such material would not be expected to retain much strength after exposure to the high temperatures of the tropics.

*Exposures to Tropical Sunlight and to a Mercury Arc Lamp.*—As oxidation of sulfur in light was known to be due to the action of rays of short wave-length, and it appeared to be fairly certain that ultra-violet light would also accelerate the aging of cotton and rubber, it was decided to make parallel exposures of various samples to sunlight in the tropics and to the light of a quartz mercury arc lamp in the laboratory. If the results of the exposures proved to be similar and to grade samples protected by different means in the same order, it would then be possible to make subsequent tests of new schemes proposed for the protection of balloon fabric without necessitating the delay and trouble involved in sending samples abroad. Mr. Porritt, then of the North British Rubber Co., arranged for the preparation of a series of 14 samples from the same delivery of scoured cotton fabric (120 g. per sq. m.) with different methods of protection. Seven of these samples were rubbered and doubled, four being steam cured and three vapor cured; the other seven were non-rubberized blanks which were subjected to the same conditions of cure, so that the effects of light on the rubber and on the cotton might be estimated separately. The nature of each sample is shown in Table II. One-half of each was sent to Somaliland and exposed for two months of summer; the other half was exposed to the light of a Cooper-Hewitt quartz mercury lamp in a specially ventilated box. When such lamps are burning there is a marked smell of ozone, which is most obvious when the arc is first struck. To eliminate the effect of traces of ozone on the rubber, and to keep the air temperature down, a chamber was built on to the end of the box in which a fan was kept running so that a steady stream of air was blown over the test-pieces. The box in which the lamp and test-pieces were arranged was about 22 cm. square, the lamp lying near the axis; the average distance from the center of a test-piece to the center of the lamp was 13 cm. To test for

ozone, some 2000 liters of air were drawn from the box when the lamp was alight and bubbled through potassium iodide; the quantity found was only 0.08 mgm., and there appeared to be about three times this amount of oxides of nitrogen. That these small quantities of ozone, etc., were insufficient to damage the rubber was demonstrated by the results obtained.

The temperature of the walls rose some 25° C. above that of the room; hence the samples in the box were at a low humidity. Moisture accelerated the loss in strength and in gas-tightness in normal exposures, so every morning, before lighting the lamp, damp cotton-wool was swabbed over the surfaces of the specimens; a separate swab was used for each test-piece and kept in a separate test-tube so that any acid formed was collected.

The exposure was continued for 20 days of 12 hours each; a second batch was exposed for 40 days. The test-pieces were soaked in water over night to remove any acid, this water being mixed with that in which the cotton-wool swabs had been kept; the tensile tests were then made after the washed test-pieces had been conditioned for 2–3 days. Permeability tests were also made, the samples being usually tested both before and after crumpling.

The tests on the samples from Somaliland were made under precisely similar conditions, except as regards the acidity tests. The swabbing had been replaced by possible early morning deposits of dew, and in the actual titration the aqueous extracts were so dark colored that it was not possible to use methyl-orange as indicator, although this had been satisfactory for the mercury arc lamp samples; phenolphthalein was used as an external indicator, and some part of the large differences in acidity may have been due to this substitution.

The results obtained are summarized in Table II.

TABLE II

| | | | Exposed to ultra-violet light | | | | | Exposed at Barbera | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Loss of Strength Per Cent | | Acidity G. $H_2SO_4$ per Sq. M. | | Permeability, Liters per Sq. M. per Day | Loss of Strength per Cent | Acidity G. $H_2SO_4$ per Sq. M. | Permeability, Liters per Sq. M. per Day |
| No. | Outer Ply | Cure | 20 Days | 40 Days | 20 Days | 40 Days | 20 Days | | | |
| 1 | Scoured | Steam | 43.7 | 51.9 | 0.14 | 0.20 | 13.5 | 52.5 | 1.26 | 240 |
| 2 | Dyed yellow | Steam | 43.2 | 49.0 | 0.09 | 0.10 | 12.5 | 35.4 | 0.98 | 0.9 |
| 3 | Dyed alizarin red on mordant | Steam | 12.5 | 29.7 | 0.02 | 0.02 | 9.5 | 24.5 | 1.38 | 1.6 |
| 4 | Scoured: Aluminum surfaced | Steam | 31.1 | 43.7 | −0.06 | 0.00 | 13.1 | 54.0 | 0.76 | 8.8 |
| 5 | Scoured | Vapor | 48.3 | 55.4 | 0.27 | 0.28 | 15.6 | 52.0 | 0.74 | 15,575 |
| 6 | Lead chromate | Vapor | 40.8 | 50.5 | 0.00 | 0.02 | 13.4 | 46.7 | 0.89 | 1.3 |
| 7 | Scoured: Aluminum surfaced | Vapor | 38.4 | 46.1 | −0.06 | −0.05 | 12.1 | 60.6 | 0.99 | 3.5,290 |
| 8 | As 1 unproofed | Steam | .. | .. | .. | .. | .. | 42.0 | .. | ..... |
| 9 | As 2 unproofed | Steam | .. | .. | .. | .. | .. | 35.7 | .. | ..... |
| 10 | As 3 unproofed | Steam | .. | .. | .. | .. | .. | 34.5 | .. | ..... |
| 11 | As 4 unproofed | Steam | .. | .. | .. | .. | .. | 28.0 | .. | ..... |
| 12 | As 5 unproofed | Vapor | .. | .. | .. | .. | .. | 60.5 | .. | ..... |
| 13 | As 7 unproofed | Vapor | .. | .. | .. | .. | .. | 51.0 | .. | ..... |
| 14 | As 6 unproofed | Vapor | .. | .. | .. | .. | .. | 23.6 | .. | ..... |

The table shows some striking general differences between the results of laboratory and tropical exposures. Although the losses in tensile strength are of the same order in both series, the gas-tightness of the specimens exposed in Somaliland had almost disappeared, while that of the material exposed to the mercury arc lamp was barely affected. This difference affords conclusive evidence that the ozone pro-

duced by the lamp was too little to be of importance, since rubber is known to be very susceptible to attack by ozonized air. Parallel with the greater deterioration of the rubber shown by the figures for the permeability of the samples from Berbera, there is a marked difference in the acidity results; although the whole of the acidity found in the open-air exposure may not have been due to sulfuric acid, most of it, as proved in preliminary tests, must have been of this nature. Hence a large proportion of the loss in tensile strength of these samples may be ascribed to the action of acid rather than to the direct effect of sunlight on the cotton.

The effect of ultra-violet light on rubbered cotton thus differs from that of tropical sunshine in that the former causes preferential deterioration of the cotton, the latter acting much more rapidly on the rubber and on the sulfur. It is not only free sulfur which is oxidized, for the vapor cured samples gave acidities of the same order as those cured in steam. These results suggest that light of wave-lengths shorter than those which occur in the solar spectrum is very efficient in the destruction of cotton, but is not so important in the oxidation of rubber and of sulfur. The differences between the two sets of conditions are so great that it is impracticable to make use of the mercury arc lamp in attempting to forecast, from laboratory exposures, the probable value of any scheme of protection. It will be observed that the order of merit assigned to the various balloon fabrics by the arc figures is in some cases quite different from that deduced from the tropical exposure; from the tensile test results, number 7 is the second best and number 2 the second worst on the ultra-violet test, whereas actually 2 appears to be second best and 7 the worst on the Somaliland exposures.

It is clear that the yellow (2, 9), and particularly the red dye (3, 10), afforded a considerable amount of protection to the cotton from the light of the sun. Lead chromate gave the most marked protection to the unproofed sample. The aluminum surfacing (which was done with a nitrocellulose medium) was valueless as judged by the tensile strength of the cotton, although it had the effect of preserving the rubber of the steam-cured sample (4); the effect on the tensile strength was largely due to the nature of the medium, for some of the No. 1 fabric which was doped with a suspension of aluminum in nitrocellulose dope to improve the gas-tightness gave a loss in strength of 0.78 per cent and an acidity equal to 2.72 g. of $H_2SO_4$ per sq. meter. The exposure was unfortunately too long to give much information as to the relative values of hot and cold vulcanization or of the different protective schemes as regards the preservation of the gas-tightness of the rubber.

During the war a number of kite balloons were sent out to the Middle East, where their life was frequently very short. One particular balloon, made with cold-cured rubber, was condemned as porous after a fortnight's use during which it spent 29 hours in the air. But hot-cured fabrics, in which the rubber was protected by means of dyes in the rubber or by aluminum doping, usually failed by reason of the loss in strength of the cotton rather than by perishing of the rubber; in some balloons which burst while still serviceable so far as gas-tightness was concerned the outer ply of cotton was found to have lost two-thirds of its strength; in one case this occurred after less than 50 days' use. No small part of this weakening was due, in certain cases, to the use of the same nitrocellulose aluminum dope which had previously been found to be unsatisfactory in sub-tropical exposures. But similar deterioration also occurred when no dope had been applied; yellow or red dyeing of the outer cotton ply had been judged to render balloons too conspicuous for use in France and a dark green dye had been adopted which afforded no protection to the cotton from the action of sunlight. In fact, Dr. Atkins came to the conclusion that in Egypt the green dye on certain balloons actually ac-

celerated the destruction of the cotton. The balloon fabrics which lasted best had aluminum printed on a thin layer of rubber over the cotton.

The virtues of aluminum finishes were very generally appreciated in connection with balloon fabrics by the end of the war. There are aesthetic and other objections to the extension of their application to articles of everyday use, but they have properties which should not be overlooked even in these days when the incorporation of antioxidants in rubber mixings is recommended. Protection of the rubber and of the cotton from the actinic light is secured by reflection, and the coefficient of reflection is not only fairly high in the ultra-violet, but is particularly high in the visible and infra-red, so that the surface is not heated so much above the air temperature as when absorbent dyes, etc., are used. In strong sunlight the temperature of a shallow vessel covered with aluminum coated fabric may be about 30° C. lower than when a dark covering is employed; the difference is significant not only

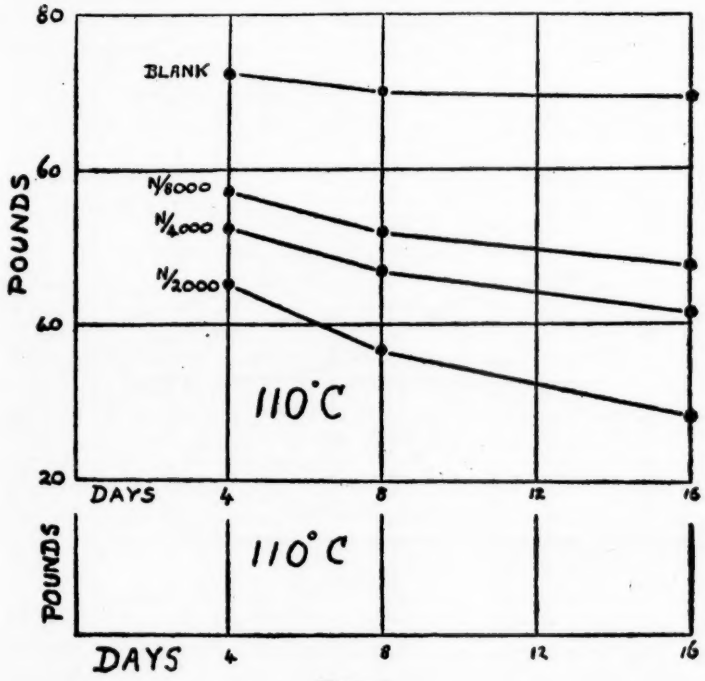


Figure 1

as regards the probable life of rubber goods in such circumstances, but as regards comfort when, for example, a water-proof garment is worn.

*The Region of the Spectrum Which Causes Deterioration.*—To find some logical basis for the selection of dyes to be used for the protection of cotton from the action of light, it is necessary to discover what rays are responsible for the deterioration. Exposures to a mercury arc lamp indicate that rays of wave lengths less than occur in sunlight are very effective; but this is not very helpful, since it is exposure to sunlight, or at least to daylight, which is of practical importance. Experiments in which non-rubberized cotton or linen was exposed behind glasses of various colors have shown that deterioration occurred almost exclusively behind screens which

transmitted the violet and near ultra-violet light and that filters which absorbed all rays of wave length lower than about 4000 Å. afforded almost complete protection. In fact, screens may usually be graded as to their efficiency in absorbing from sunlight the rays deleterious to cellulose by comparing their opacity by means of Velox or bromide paper placed behind them in a photographic printing frame using either sunlight, incandescent gas, or electric light. This useful practical result was first noticed after making tensile tests on a number of samples of aeroplane fabric taken from the wings of planes which had seen service in Egypt; the samples included doped pieces which had been merely varnished with a colorless varnish, others which had been covered with pigmented dopes and others taken from the identification circles; the order of strength was the same as the order of opacity as judged by printing tests, not as judged by visual examination.

The test is simple and appears to suggest that the maximum of deterioration is produced by the same rays which cause the maximum effect on silver bromide, *i. e.*, by rays at the lower end or just below the lower end of the visible spectrum.

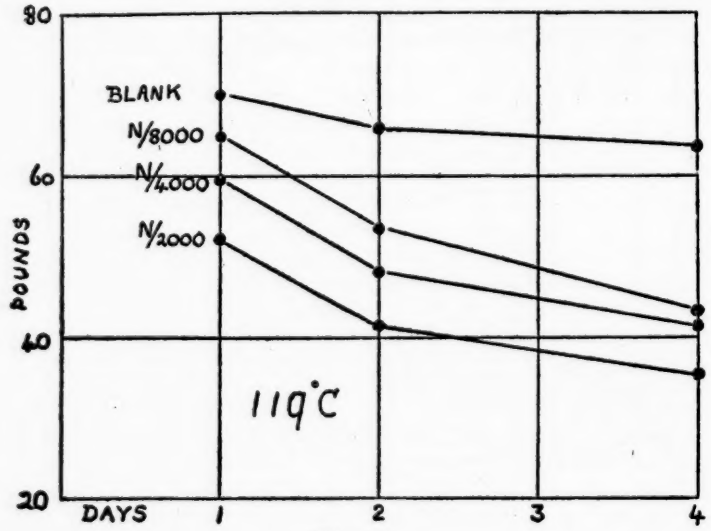


Figure 2

Unfortunately the evidence is not complete; it is known that light of wave length less than 3000 Å. is very active in destroying cellulose, though the effect on silver halides diminishes as the wave length is reduced, and it is possible that the apparent maximum is due to the fact that the energy in the solar spectrum decreases rapidly below 4000 Å., and that the screens which happen to have been used absorb the more active radiation of short wave length (3000–3500 Å.) more completely than that nearer to the visible. It is thus conceivable that if a dye applied to cotton had an absorption band with its head at 4000 Å., and was relatively transparent below 3500 Å., it might not afford very good protection. It has been found, however, that deterioration of cotton occurs when samples are placed in glass tubing and exposed to sunlight and Dr. Ramsbottom showed that the rate of deterioration is not appreciably greater when silica tubing is used; this fact affords some evidence that the radiation of wave length less than 3300 Å. present in sunlight is not of much importance in this connection, if it may be assumed that the silica tubing was not much less transparent than the glass in the other parts of the spectrum.

Definite and exact information regarding the distribution of destructive power in the spectrum should be obtainable from exposure of cotton in the plate-holder of a spectroscope. Dr. Aston attempted the experiment, using sewing thread of which the mean breaking stress was known and determining the strength of each thread after exposure to a portion of the spectrum of a quartz-mercury arc for about a month. The extent of deterioration was, however, so small that he could not do more than recognize that some attack had occurred where the lines in the ultra-violet part of the spectrum had fallen. The writer has recently been repeating Aston's experiment under rather different conditions to see whether differences in the exposed cotton can be detected by the very sensitive criterion of the measurement of viscosity of the cotton in cuprammonium solution. Miss Hadfield and the writer found that such measurements could be made to show a definite loss of viscosity when cotton had been exposed to bright sunshine for one day. The sensitivity of the method may be judged from the fact that the strength after 340 hours of sunshine had fallen for coarse fabric by 24 per cent, while the viscosity fell from 470 to 12 poises; for the fine fabric the viscosity fell from 200 to 1.7 poises, while the strength dropped by 37.5 per cent. The sensitivity is much higher for the early stages. It may be necessary, however, owing to the small weight of material available in the present experiments, to use rather less sensitive conditions of viscometry.

The deterioration of cotton, like that of rubber, on exposure to sunlight, is essentially a process of oxidation. The cotton acquires the reducing properties characteristic of oxy-cellulose, but there is no marked increase, at any rate in the early stages, in the affinity for methylene blue. Birtwell, Clibbens, and Ridge (*J. Text. Inst.*, **16T,** 13 (1925)) have shown that the properties of oxy-cellulose depend on the alkalinity or acidity of the bleaching bath, when the oxidation is effected by means of hypochlorite solutions; the relation between the reducing properties and the methylene-blue absorption of cotton exposed to sunlight is similar to that observed by them for cotton bleached with chlorine water. By conducting the exposure in sealed glass tubes it has been found that practically no change occurs in the absence of oxygen. It has been observed at the National Physical Laboratory that during the oxidation which takes place when the tubes are filled with oxygen a considerable quantity of carbon dioxide is produced, together with smaller amounts of carbon monoxide, hydrogen and methane. The minor products are probably due to light of the shortest wave lengths transmitted by the glass, since these rays produce the same gases from sugars. There is also present in the tubes in which cotton has been oxidized a small amount of a product having a sharp smell like an aldehyde, but hitherto it has not been possible to identify it; the smell disappears when an aqueous solution is stored, and is replaced by a more pleasant ethereal smell.

*The Effect of Traces of Acid on Cotton.*—In view of the high temperatures to which rubbered cotton is exposed during vulcanization with steam, the possible presence of traces of acid in the cloth is obviously of great importance. A short investigation was made at the National Physical Laboratory some years ago on the rate at which loss in strength occurred in samples of cotton and linen which after thorough scouring and washing had been immersed in dilute solutions of sulfuric acid; after drainage the excess of liquid was removed by pressure between sheets of filter paper and the impregnated cloth allowed to dry in the air. The acid solutions were, respectively, $N/2000$, $N/4000$ and $N/8000$, and it was estimated that the treated cloth contained 0.31, 0.16 and 0.08 per cent of acid. Comparative samples were then heated in an electric oven at 110° C., 119° C. and 127° C. for times ranging from 1 to 16 days and the rate of loss of strength determined. In order to avoid correc-

tions for humidity effects, the tensile tests were carried out on soaked test-pieces. In the blank determinations on samples heated together with the acid samples, it was considered advisable to impregnate the cloth with $N/1000$ sodium carbonate solution since acid had been used in the preliminary scouring. The changes are shown in the three series of curves, Figs. 1–3.

In the range covered by these experiments it appears that the rate of loss in strength at a given temperature becomes about one and a half times as great when the concentration of the acid in which it has been immersed is doubled; since the weight of acid retained is also approximately doubled, this means that the rate of loss in strength is roughly proportional to the weight of acid in the cloth. With a given acidity the rate of the reaction is doubled for a rise in temperature of about 8° C. With certain assumptions as to the nature of the reaction and with a dangerous extrapolation for the effect of temperature, it has been calculated that cotton fabric which has been dipped in $N/8000$ sulfuric acid and dried by pressure between absorbent material should show a loss of 5 per cent of its strength after 1000 years at 30° C.

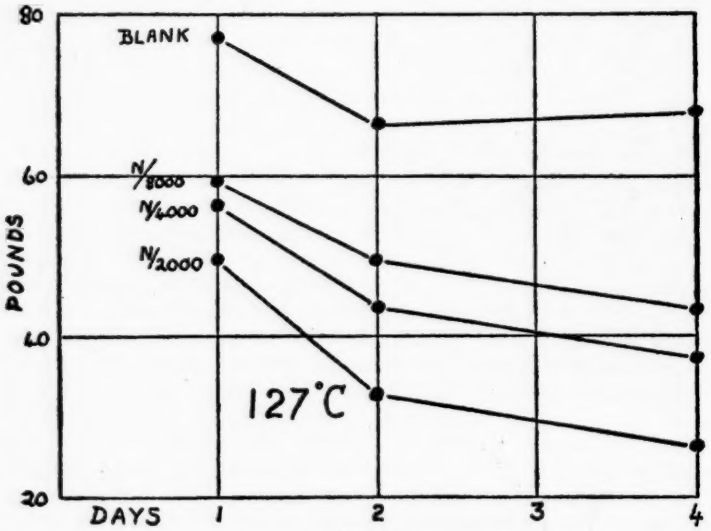


Figure 3

In the course of these tests it was found that the test included in the British Engineering Standards Association specification for cotton for aircraft purposes gave no positive indication of acidity when cotton had been dipped in acid weaker than $N/4000$ and allowed to dry. The test consisted, as may be remembered, in extracting a 6 inch square of the cotton twice with boiling water and titrating the extract with centinormal sodium hydroxide solution, using phenolphthalein as indicator. Spotting the fabric with lacmoid solution gave definite results up to a dilution of $N/10{,}000$. These limits correspond with percentages of about 0.016 and 0.005, respectively, of sulfuric acid in the cloth. A year or two later Coward and Wigley (*J. Text. Inst.*, **13T**, 121 (1922)) made an investigation into methods of estimating acidity and alkalinity in cotton fabrics. The limit for the British Engineering Standards Association test agreed fairly well with the writer's, but they gave the limit for spotting with lacmoid as 0.03 per cent for a well-bleached cloth;

some of the difference may conceivably be due to different strengths of indicator solutions. They showed that titration near the boiling point in the presence of the fabric with $N/50$ sodium hydroxide solution and phenolphthalein gave results accurate to about 0.01 per cent of sulfuric acid. It appears, however, that this accuracy is only just sufficient to ensure freedom from tendering on long exposure. Higher sensitivity is obtained, according to Coward and Wigley, by spotting with a saturated solution of methyl red in water, which gives a positive result when there is 0.005 per cent of acid present.

In this connection reference may be made to some experiments described by Coward, Wood, and Barrett (*J. Text. Inst.*, **14T**, 520 (1923)), who found that heating for 10 minutes between copper plates at 100° C. produced a loss in strength averaging some 13 per cent in fabric containing 0.05 per cent of its weight of hydrochloric acid; a similar loss occurred with 0.01 per cent of acid at 120° C. Their results confirm and amplify observations made by Lester (*J. Soc. Chem. Ind.*, **34**, 935 (1915)).

In a more recent paper Clibbens and Geake (*J. Text Inst.*, **18T**, 168 (1927)) found quantities of sulfuric acid up to 0.01 per cent in technically bleached or scoured cotton. They drew attention to the fact that when dilute sulfuric acid had been allowed to dry on cotton and attack allowed to proceed by raising the temperature, a proportion of the acid was retained in such a form that it could not be removed by washing with water or even by boiling with 1 per cent sodium hydroxide solution for 6 hours.

The destruction of cotton in rubber goods by the action of moulds and bacteria is of much less importance than that involving effects of light and acidity. The presence of a water-proof layer of rubber may, however, favor the prolonged retention of high humidity in the cotton, a factor which has been shown by several investigators to be of crucial importance in the growth of organisms on cotton. That troubles due to this cause are not normally acute may be due partly to the more rapid attacks made by acid and by light, partly to an inhibitory effect of sulfur or of residual solvent on the growth of any organisms.

[Reprinted from India Rubber Journal, Vol. 78, No. 9, pages 316–318, August 31, 1929.]

# The Relationship between Forces and Deformations

## With Special Reference to Rubber[1]

R. Ariano

### Introduction

A matter of great interest and importance in the study of stress-strain relationships is the problem of expressing the behavior of a material in terms of a few constant coefficients, each having a definite physical significance and depending only on the nature of the material. The following is a contribution toward this problem, with special reference to rubber and the analogy between rubber and other materials.

### 1. Classification of Types of Deformation

Although sharp lines of demarcation cannot always be drawn between the different types, in the case of rubber there appear to be two extremes each having absolutely typical properties, namely, raw rubber and vulcanized rubber.

Setting aside any arbitrary definitions of the solid state (such as that which defines a solid as an extremely viscous liquid), the following classification of types of deformation may be put forward:

(i) Elastic deformations (disappear as soon as the stress is removed).

(ii) Viscous or sub-permanent deformations (disappear more or less rapidly—but always within a relatively short—after removing the stress).

(iii) Permanent deformations (do not disappear on removing the stress—at any rate of absence of temperature changes, etc.).

This classification brings together three particularly interesting types of deformation, each of which occurs in a predominating degree in certain particular cases.

The more detailed classifications which have been proposed do not seem to be applicable to so wide a range of materials.

### 2. Classification of States of Aggregation

In a previous paper (Ariano, *Il Nuovo Cimento*, Mar., 1928; *India Rubber J.*, **76**, 207 (1928)) it was shown that if masticated raw rubber at ordinary temperatures is subjected to a constant stress exceeding a certain limiting value (the "fluidification stress"), deformation proceeds continuously until the test-piece breaks. This behavior is observed also in metals, where the "creep stress" or "viscosity" limit corresponds to the fluidification stress of rubber.

Hot masticated rubber shows zero fluidification stress, but at ordinary temperatures, especially after certain treatments (calendering, stretching, or allowing to stand), it may attain considerable values; it is also increased by adding compounding ingredients, but decreases with rise of temperature. The temperature at which the fluidification stress becomes zero may be called the "point of viscous fusion" (*cf.* the "Schmelzlinie" of Feuchter), and that at which it becomes sensibly equal to the breaking stress may be called the "solidification point."

[1] *Il Nuovo Cimento*, March, 1929.

This behavior of raw rubber suggests the following classification of states of aggregation:

(i) Solid state: below the "solidification point." Deformation is completely elastic and is propagated very rapidly. The material possesses a definite breaking stress.

(ii) Plastic state: between the "solidification point" and the "point of viscous fusion." There is no well-defined breaking stress, and the stress-strain relationships are a function of time. All three types of deformation are encountered, subpermanent deformation being always prominent.

(iii) Liquid viscous state: above the "point of viscous fusion" (but below the true melting point). Even the smallest stress produces flow. Deformation is propagated very slowly, and there is no true stress-strain relationship. Elastic deformation is practically absent, permanent deformations being predominant.

(iv) Liquid state, with zero viscosity. The term "deformation" no longer has any significance.

When considering the structure of rubber, as distinct from its stress-strain relationships, it may be necessary to include the "mesoform" state between the plastic and liquid states (see in this connection Mayr, *Il Nuovo Cimento*, February, 1928, *Rivista*, XXV[a]), especially as the mesoform state is peculiar to unsaturated long-chain organic compounds, of which rubber is an example. Also, the assumption of a "liquid crystalline" state in rubber might help to explain the "transition points" of raw rubber, *e. g.*, that between 60 deg. and 80 deg. C.

### 3. The Structure of Raw Rubber

The fibrous structure and crystalline X-ray diffraction pattern acquired by raw rubber on stretching, and the disappearance of both these effects on heating have been explained by assuming the existence of two phases, each a polymer of isoprene, *viz.*, phase, containing a small number of isoprene molecules, and $\beta$ phase, containing a larger number; the latter is assumed to be swollen by the $\alpha$ phase and to form a kind of network. Rise of temperature converts $\beta$ into $\alpha$.

This conception may be applied to the above-described classification of states of aggregation as follows:

(*a*) At low temperatures (below 0 deg. C.) raw rubber consists of granules of $\beta$ swollen in $\alpha$ and cemented together by $\alpha$; the material, however, consists mainly of $\beta$ phase. This structure is characteristic of raw rubber in the "solid" state.

(*b*) At ordinary temperatures (plastic state) the $\beta$ granules are considerably swollen by the $\alpha$ phase. The fluidification stress is that stress which, acting on the granules, produces a transverse pressure just sufficient to squeeze out, wholly or partly, the absorbed $\alpha$ phase (*cf.* action of pressure in expressing liquid from a gel or sponge). When this occurs the rubber also begins to show a crystalline X-ray diagram, which arises not from the presence of true crystals, but from the orientation of the $\beta$ granules and of the intervening viscous filaments of $\alpha$ phase. The Joule effect is probably due to the heat evolved by the liberation of the $\alpha$ phase from the granules.

(*c*) With rise of temperature the amount of $\beta$ phase decreases, and the liquid viscous state is reached.

The above considerations will explain certain other phenomena such as calender grain; the lack of "nerve" in raw rubber plastified by heat is due to the conversion of solid $\beta$ into viscous $\alpha$ phase. The temperature at which $\beta$ is completely converted into $\alpha$ probably represents one of the "transition points" of raw rubber. The conversion of $\beta$ into $\alpha$ is accompanied by absorption of heat.

### 4. The "Fluidification Stress" of Metals

The fluidification stress or "viscosity limit" of metals is usually very high (of the order of 10 to 100 kg./mm.$^2$—stress calculated on *actual* section) at ordinary temperatures, but may decrease to 1 kg./mm.$^2$ or less at high temperatures, and as the fluidification stress of raw rubber may be as high as 0.5 kg./mm.$^2$ it is clear that there is no break in continuity in passing from rubber to metals, the main difference lying in the temperature range over which plastic properties are exhibited.

When raw rubber is subjected to the action of a constant tensile load, the time/extension curve has the form characteristic of substances in the plastic state (including metals at elevated temperatures), that is, extension proceeds at first very rapidly (instantaneously with most plastic materials), but the rate of extension later decreases and finally assumes a constant value (either zero or finite). From this follows the important conclusion that for a material in the plastic state, "stress-strain relationships," as ordinarily understood, have no meaning or can at best be only very rough approximations.

### 5. The Deformation of Vulcanized Rubber

In a well-vulcanized rubber-sulfur mixing the fluidification stress practically coincides with the breaking stress, and the sub-permanent set is very small; the rubber is therefore in the "solid" state. With low-grade mixings made of reclaim plus large amounts of mineral fillers, however, a load much below the normal breaking load will ultimately cause rupture if it acts continuously; also, the sub-permanent set is very high; the material is, therefore, "plastic" rather than "solid."

*Experiments on Sub-Permanent and Permanent Set.*—Tests were made with cords of a well-vulcanized rubber-sulfur mixing (the results are equally applicable to mixings containing also accelerators, antioxidants, and small amounts of zinc oxide).

The residual extension of a cord, after being stretched and then released, was found to decrease rapidly during the first two to four minutes (disappearance of sub-permanent set), after which it remained practically constant (permanent set). The observed permanent sets were as follows:

| | Permanent set, % |
|---|---|
| Stretched for 1 hour at 500 per cent elongation | 5 |
| Stretched for 5 hours at 500 per cent elongation | 9.5 |
| Stretched for 1 hour under load giving initially 500 per cent elongation | 8 |
| Stretched for 5 hours under same load | 9.7 |
| Stretched for 16 hours under same load | 11.5 |

The permanent set depends on the period of stretching, and may, therefore, be ascribed mainly to a very slow molecular rearrangement. Constant load gives a higher set than constant elongation. This is not surprising, because rubber subjected to a constant load ($P_o$) gradually stretches, so that after a time the load ($P_t$) corresponding to the initial elongation may be much less than the load ($P_o$) which initially produced that elongation. The difference between $P_t$ and $P_o$ (expressed as a percentage of $P_o$) may be called the "loss of tension;" the magnitude of this loss is illustrated by the following figures for a rubber-sulfur mixing:

| | | | | | |
|---|---|---|---|---|---|
| % Elongation: initial | 101 | 203 | 303 | 366 | 541 |
| % Elongation: after 18 hours under load | 118 | 231 | 341 | 400 | 583 |
| Loss of tension (%) | 9.55 | 9.65 | 15.5 | 15.7 | 27.9 |
| Permanent set (%) 30 mins. after removing load | 5 | 6.5 | 8 | 9 | 13 |

The "loss of tension," which may be nearly 50 per cent in some cases, is obviously a constant of great practical importance.

When a rubber cord was stretched to 500 per cent elongation, and the load then reduced until the elongation was about 120 per cent, no change in length occurred on leaving the rubber for some time under the residual load; under a smaller residual load, however, the cord slowly contracted, whereas under a larger load it gradually extended again. These results are explicable by assuming that subjection to any given stress eventually produces a state of structural equilibrium, which, however, is reached only after a considerable time; similarly, on removing the stress the original structure is slowly recovered. If a stress is applied only for a short time (so that structural equilibrium is not reached) and the stress is then reduced to a value $P$, the behavior of the rubber when left under the stress $P$ will depend upon whether its structure at the time of reducing the stress corresponded to the equilibrium condition for a stress greater or less than $P$.

*Effect of Prolonged Stretching.*—Rubbers of the "pure mixing" type were stretched to 50 per cent and 150 per cent elongation at ordinary temperatures in the dark for 83 days. The permanent set, however, was still only small (2 to 15 per cent) and the breaking elongation after stretching did not differ much from the original value, although the tensile strength was rather lower.

In another experiment rubber cords, stretched for 25 days at elongations ranging up to 150 per cent, showed a decrease in tensile strength, this decrease being greatest for the samples stretched to 10–25 per cent; no explanation of this latter point is offered.

*Effect of Stretching and Exposing to Light.*—When rubber cords, stretched to constant elongation, were exposed to light, either in air, nitrogen, or a vacuum, the stress-strain curve moved toward the elongation axis, *i. e.*, the rubber appeared to become softer; this, however, was only the case when the stresses were calculated on the *original* cross-section; when they were calculated on the cross-section *after* exposure, the initial part of the stress-strain curve coincided approximately with that of the untreated rubber, but the later part was found to bend over more sharply toward the stress axis, so that the exposed sample appeared tougher. A similar change in the shape of the curve was observed in compression tests. This effect was found with all types of mixing, whether transparent or opaque, with or without antioxidants. In all cases the tensile strength was lowered, and in presence of air superficial oxidation and cracking occurred.

*Effect of Heating in Nitrogen.*—The following results were obtained on heating a rubber-sulfur mixing, stretched to constant elongation, in a current of nitrogen:

(*a*) The permanent set after heating was small and did not vary greatly with the temperature or duration of heating, but increased rapidly with increase in the elongation (see following results for samples heated at 72 deg. C.):

| | | | | |
|---|---|---|---|---|
| Elongation during test (%) | 10 | 50 | 150 | 300 |
| Permanent set (%) | 2 | 8.7 | 12 | 21 |

(*b*) During 12 days' heating at 72 deg. C., the tensile strength did not change markedly, provided the elongation during the heating was not excessive (say below 400 per cent). The stress-strain curve, however, showed the same bending toward the stress axis as in the experiments on exposure to light (see above); the breaking elongation, therefore, decreased somewhat. This change in the stress-strain curve may occur in some rubber articles (*e. g.*, belts) during use.

*Hysteresis Cycles.*—Hysteresis cycles indicate the rate at which sub-permanent set arises (during increasing load) and disappears (during decreasing load); the speed of the cycle in hysteresis tests is, therefore, highly important. Hysteresis is not peculiar to rubber, for it represents a generally known phenomenon observed, for instance, in metals. The most significant work on the hysteresis of rubber is that of Bouasse and Carriere.

The shape of the stress-strain curve obtained with decreasing load ("return curve") depends closely on that of the original "loading curve," and on the part of the latter from which the return curve is started; the nature of this dependence is more exactly as follows:

(*a*) If the upper part of the loading curve is but slightly inclined to the stress axis (*i. e.*, if the "slope" or "type" is low), and the return curve is started from this upper part of the loading curve, the return curve runs almost parallel to the stress axis until the load reaches a very small value, when the curve bends sharply and runs almost parallel to the elongation axis. The hysteresis loop in this case has a very large area.

(*b*) If the upper part of the loading curve is considerably inclined to the stress axis, or if the return curve is started from a point lower down the curve, the return curve runs initially at a considerable inclination to the stress axis and follows the loading curve more closely than in case (*a*). The area of the hysteresis loop is therefore small.

(*c*) The shape of the loading curve in the second hysteresis cycle depends on whether the first return curve is (i) continued down to zero load, or (ii) stopped short at, say, 100 or 200 per cent elongation. In case (i) the second loading curve closely resembles the first, especially if the rubber is allowed to rest before starting the second cycle. In case (ii) the second loading curve deviates markedly from the first, being nearer the elongation axis. In all cases the second return curve lies close to the first return curve.

(*d*) Successive hysteresis loops decrease in area. By far the greatest difference (both in area and in the position of the stress-strain curve) occurs between the first and second cycles, that is, the rubber tends to accommodate itself to the stretching treatment, and with pure mixings an approximate state of equilibrium is reached after three to five cycles.

(*e*) If stress is calculated on the *actual* (stretched) cross-section, both the loading and return curves are of the hyperbolic type, but the latter has the sharper curvature.

The alteration in the stress-strain properties of vulcanized rubber by subjection to cycles of traction has its analogue in metals, though in the latter case the material is hardened, whereas rubber is softened. This may be explained by assuming that in metals internal tension reduces the size of the crystals or leads to the formation of amorphous material, whereas in vulcanized rubber it tends to convert an isotropic amorphous material into one approaching the crystalline state.

## Summary

From an examination of the various possible types of deformation in raw and vulcanized rubber it is shown that the behavior of these materials is in no way exceptional or radically different from that of metals, and that apart from the order of magnitude of the deformations there is no reason for considering the behavior of rubber as being outside the sphere of ordinary mechanics.

It is shown how certain recent theories concerning the structure of raw rubber explain its physico-mechanical behavior, and the influence of certain factors on the stress-strain properties of vulcanized rubber is qualitatively examined.

[Reprinted from India Rubber Journal, Vol. 78, No. 10, pages 351–353, September 7, 1929.]

# The Coefficients of Friction between Rubber and Other Materials

## Frictional Grip of Rubber-Tired Wheels

R. Ariano[1]

### 1. Experimental Method

The static friction between rubber tires and other surfaces was measured by placing the tire on a wheel (not free to rotate) fixed to a beam pivoted at one end. The tire rested on a horizontal iron plate free to move horizontally but not vertically, and was pressed on to this plate with a predetermined force by loading the beam. A horizontal force was then applied to the plate and increased gradually until it reached a value ($F$) just sufficient to overcome the friction between the tire and the plate, and thus caused the latter to move. If the load on the wheel is $L$, and the weight of the wheel and tire is $W$, then the "gripping friction" of the tire $f = F \div L$, while the true coefficient of friction $f^1 = F \div (L + W)$; the former, however, is of more practical interest. Tests were made with the force $F$ acting: (i) in the plane of the wheel (direction of travel) and (ii) perpendicular to this plane (corresponding to the forces involved in lateral skidding). Except where otherwise stated, the horizontal supporting plate was of iron, but in some experiments this was replaced by a slab of an actual road-surfacing material.

### 2. Tests on New Pneumatic Tires

(i) *Coefficients of Friction in Direction of Travel.*—The following results (Table 1) were obtained with two 820 × 120 Pirelli tire covers, identical except that one had the usual tread pattern and the other a smooth tread.

TABLE I

| Inflation Pressure Kg./Cm.$^2$ | Load on Wheel, Kg. | Smooth Tire | | Patterned Tire | |
|---|---|---|---|---|---|
| | | $f$ | $f^1$ | $f$ | $f^1$ |
| 2 | 212 | 0.63 | 0.50 | 0.57 | 0.46 |
| 3 | 212 | 0.63 | 0.50 | 0.59 | 0.47 |
| 4 | 212 | 0.61 | 0.49 | 0.58 | 0.46 |
| 5 | 212 | 0.60 | 0.48 | 0.58 | 0.46 |
| 5 | 300 | 0.61 | 0.51 | 0.60 | 0.50 |

The coefficient of friction is practically independent of the load and inflation pressure, and the smooth tire shows a higher friction than the patterned tire; both these conclusions have been confirmed by many other tests.

Under a given load the patterned tire suffers a greater compression and has a smaller effective area of contact than the smooth tire. Both these factors would be expected to give the patterned tire the higher coefficient of friction. As this is not actually the case, the observed difference in coefficient of friction cannot be directly related to differences in compressibility or area of contact with the supporting surface, but is more probably due to differences in the distribution of local pressures and deformations.

[1] From *Il Politecnico*, No. 5, 1929.

The results in Table II were obtained with 30 × 5.25 "Superflex" covers.

TABLE II

| Supporting Surface | Iron Plate | Cement-Sand Mixture, Clean | Cement-Sand Mixture, Covered with Mud |
|---|---|---|---|
| Smooth tread | $f$.....0.58 | 0.64 | 0.37 |
| | $f^I$.....0.52 | 0.58 | 0.33 |
| Patterned tread | $f$.....0.54 | 0.54 | 0.41 |
| | $f^I$.....0.49 | 0.49 | 0.37 |

These results show clearly how the tread pattern increases the grip of the tire on a muddy surface, although it does not on a clean surface.

The influence of the type of tread mixing, type of road surface, and especially of the presence of mud or dust is illustrated by the figures in Table III.

TABLE III

COEFFICIENT OF FRICTION ($f$)

| Surface | American 30 × 6 Tire | Pirelli 30 × 6 Tire |
|---|---|---|
| Cement-sand mixture, dry | 0.56 | .. |
| Cement-sand mixture, with light covering of dust | 0.53 | .. |
| Cement-sand mixture, with thick covering of dust | 0.38 | .. |
| Cement-sand mixture, with covering of mud | 0.46 | .. |
| Compressed natural asphalt,* dry | 0.63 | 0.74 |
| Compressed natural asphalt,* wet | 0.51 | 0.62 |
| Macadam, surfaced with bitumen,* dry | 0.65 | 0.68 |
| Concrete* | 0.65 | .. |
| Concrete, surfaced with Spramex | 0.45 | .. |
| Concrete, covered with mud | 0.33 | .. |

* Taken from an actual road surface.

Very large tires (*e. g.*, 34 × 7) show a lower coefficient of friction than smaller tires (*e. g.*, 30 × 6, 30 × 5.25) of similar design and material. This may be due to the larger tire being less easily deformed by the horizontally applied stress.

(*ii*) *Coefficients of Friction Perpendicular to the Direction of Travel* ($f_n$ *and* $f_n^I$).—The tires with plain and patterned treads already mentioned (see Table II) gave the results shown in Table IV.

TABLE IV

| Inflation Pressure, Kg./Cm.² | Load on Wheel, Kg. | Iron Plate | | Cement-Sand Mixture | | | |
|---|---|---|---|---|---|---|---|
| | | | | Clean | | Muddy | |
| | | Plain | Pattern | Plain | Pattern | Plain | Pattern |
| | | | | $f_n$ | | | |
| 2 | 212 | 0.86 | 0.74 | 0.86 | 0.86 | 0.53 | 0.69 |
| 2 | 300 | 0.86 | 0.75 | 0.82 | 0.79 | 0.52 | 0.68 |
| 3 | 212 | 0.90 | 0.74 | 0.86 | 0.86 | 0.54 | 0.69 |
| 3 | 300 | 0.90 | 0.75 | .. | .. | .. | .. |
| 4 | 300 | 0.90 | .. | .. | .. | .. | .. |
| | | | | $f_n^I$ | | | |
| 2 | 212 | 0.77 | 0.67 | 0.77 | 0.77 | 0.48 | 0.02 |
| 2 | 300 | 0.78 | 0.68 | 0.75 | 0.72 | 0.47 | 0.62 |
| 3 | 212 | 0.81 | 0.67 | 0.77 | 0.77 | 0.49 | 0.62 |
| 3 | 300 | 0.82 | 0.68 | .. | .. | .. | .. |
| 4 | 300 | 0.82 | .. | .. | .. | .. | .. |

These coefficients are markedly higher than those in the direction of travel, but, like the latter, are not greatly dependent on the load or inflation pressure, and again the tread pattern tends to lower the friction on clean surfaces and increases it on muddy surfaces.

Results on various road surfaces are shown in Table V.

TABLE V

COEFFICIENT OF FRICTION ($f_n$)

| Surface | American 30 × 6 Tire | Pirelli 30 × 6 Tire |
|---|---|---|
| Cement-sand mixture, dry | 0.70 | 0.91* |
| Cement-sand mixture, covered with mud | 0.60 | 0.60 |
| Cement-sand mixture, covered with more fluid mud | 0.56 | .. |
| Cement-sand mixture, with light covering of dust | .. | 0.87 |
| Cement-sand mixture, with thick covering of dust | .. | 0.56 |
| Macadam, surfaced with bitumen | 1.02† | 1.12† |
| Compressed asphalt, dry | 0.96 | 1.06 |
| Compressed asphalt, wet | 0.90 | 0.96 |

* Tire tread cleaned with benzine.
† Not changed by slightly wetting the surface.

Deformable road surfaces (*e. g.*, bituminized macadam), which retain an imprint of the tread pattern, give high coefficients, as would be expected. The influence of the fluidity of the mud will be noted. With the thin mud, and also on the asphalt, the friction tended to decrease with increasing load on the wheel.

Giant pneumatics again give lower coefficients of friction than smaller tires, as in the case of friction in the direction of travel.

### 3. Semi-Pneumatic (Cushion) Tires

The following results were obtained with Pirelli semi-pneumatic tires, the three tread mixings used being denoted by I, II, and III.

(*i*) *Coefficients of Friction in Direction of Travel.*—Table VI gives the result obtained on a dry surface of the cement-sand mixture; the first figure of each pair represents $f$ and the bracketed figure $f^1$. All the new tires except the 120 × 670 had the same tread pattern; the used tires had the pattern worn off.

TABLE VI

| Tire Size | Mixing | Load on Wheel (Kg.) 500 | 750 | 1100 |
|---|---|---|---|---|
| New tires: | | | | |
| 120 × 720 | I | 0.65 (0.60) | 0.55 (0.48) | 0.50 (0.49) |
| 120 × 720 | II | 0.65 (0.56) | 0.59 (0.53) | 0.51 (0.50) |
| 120 × 670 | I | 0.65 (0.57) | 0.56 (0.51) | 0.56 (0.53) |
| 140 × 720 | I | 0.45 (0.37) | 0.44 (0.38) | .. .. |
| 175 × 670 | I | 0.44 (0.37) | 0.41 (0.36) | 0.39 (0.35) |
| Used tires: | | | | |
| 120 × 720 | I | 0.61 (0.53) | 0.59 (0.53) | 0.56 (0.52) |
| 140 × 720 | I | 0.60 (0.50) | 0.56 (0.50) | 0.53 (0.49) |
| 120 × 720 | III | 0.56 (0.48) | 0.55 (0.50) | 0.51 (0.48) |
| 140 × 720 | III | 0.67 (0.56) | 0.61 (0.49) | .. .. |

There is here no relationship between the type of tread pattern and the coefficient of friction, but this coefficient is influenced by the composition of the mixing, its rigidity being the deciding factor (III is stiffer than I and II). The friction tends to be lower with the wider tires and with higher loads.

As with pneumatic tires, no direct relationship was found between the coefficient of friction and either the compressibility of the tire or its area of contact with the supporting surface.

The coefficient of friction for semi-pneumatics is about the same as for pneumatics of similar dimensions.

Tests on various surfaces are reported in Table VII, the load on the wheel being 500 kg.

TABLE VII

| Surface | 175 × 670 Tire | | 120 × 670 Tire | |
|---|---|---|---|---|
| | $f$ | $f^1$ | $f$ | $f^1$ |
| Macadam, surfaced with bitumen..... | 0.70 | 0.59 | 0.78 | 0.68 |
| Compressed asphalt..... | 0.65 | 0.55 | .. | .. |
| Cement-sand mixture, muddy..... | .. | .. | 0.53 | 0.47 |

Again the softer surfaces give high coefficients of friction and the presence of mud lowers the friction.

(*ii*) *Coefficients of Friction Perpendicular to Direction of Travel.*—The tires already described (Table VI), when tested on the cement-sand mixture, gave the results shown in Table VIII.

TABLE VIII

| Tire Size | Mixing | Load on Wheel 212 Kg. | Load on Wheel 300 Kg. |
|---|---|---|---|
| New tires: | | | |
| 140 × 720 | I | $f_n^I = 0.52$ | 0.52 |
| 120 × 720 | II | $f_n^I = 0.69$ | 0.67 |
| Used tires: | | | |
| 120 × 720 | I | $f_n = 0.83$ | .. |
| 120 × 720 | III | $f_n = 0.83$ | .. |
| 140 × 720 | I | $f_n = 0.82$ | .. |
| 140 × 720 | III | $f_n = 0.81$ | .. |

These results show that $f_n$ is always greater than $f$, and that the former increases when the tire is used. The friction is about the same as for pneumatics of similar size, and is not much influenced by the load or the type of mixing.

### 4. Solid Rubber Tires

Owing to limitations of apparatus, tests were made on small rubber-tired wheels about 10 inches in diameter. The following conclusions were drawn: (i) the tread pattern lowers the coefficient of friction (in the direction of travel) on clean cement, but increases it on muddy cement; (ii) probably owing to the comparatively slight deformability of the tires, the coefficients in the two directions ($f$ and $f_n$) do not differ sensibly, both being about 0.45 to 0.6; (iii) variations in the rubber mixing do not alter the coefficient of friction by more than 0.1.

### 5. Iron-Tired Wheels

The results shown in Table IX were obtained with a smooth iron-tired wheel.

TABLE IX

| Load on Wheel | 300 Kg. | | | | 400 Kg. | | 500 Kg. | |
|---|---|---|---|---|---|---|---|---|
| | $f$ | $f^1$ | $f_n$ | $f_n^I$ | $f$ | $f^1$ | $f$ | $f^1$ |
| On iron plate..... | 0.18 | 0.17 | .. | .. | 0.20 | 0.19 | 0.17 | 0.16 |
| On cement-sand mixture, dry.... | 0.29 | 0.28 | 0.37 | 0.35 | 0.24 | 0.23 | .. | .. |
| On cement-sand mixture, muddy | 0.37 | 0.36 | 0.45 | 0.42 | 0.4 | 0.38 | .. | .. |
| On concrete surfaced with Spramex..... | 0.51 | 0.48 | .. | .. | .. | .. | .. | .. |
| On compressed asphalt, dry..... | 0.40 | 0.38 | .. | .. | 0.41 | 0.40 | .. | .. |
| On compressed asphalt, wet.... | 0.53 | 0.5 | .. | .. | .. | .. | .. | .. |

The friction is considerably influenced by the softness of the supporting surface; on the asphalt the wheel made an impression a few millimeters deep, and this makes

it difficult to assign a definite value to the coefficient of friction. Although iron-shod wheels show a much smaller friction than rubber-tired wheels, mud or water may increase the friction with the former.

### 6. Distribution of Deformations in the Rubber Tires During the Tests

The deformations induced in the tire by the horizontal force applied to the supporting surface were examined by marking a network of lines on the tire side-wall before making the test. With a 34 × 7 pneumatic tire subjected to a horizontal force (insufficient to cause slipping) applied in the direction of travel, the side-walls above the area of contact with the supporting surface showed, on the side nearest the applied force, a horizontal compression and a vertical stretching, while on the side farthest from the force they showed exactly the opposite changes (the vertical compression, however, was very slight). These deformations extended only about halfway up the side-wall. A 720 × 120 semi-pneumatic showed similar results, except that the deformations extended across the whole width of the side-walls.

In the case of the pneumatic tire, when the horizontal force was applied perpendicular to the plane of the wheel, the side-wall toward the force showed a vertical stretching and the opposite side-wall a contraction.

The variation in magnitude and distribution of these deformations may account for some of the anomalies observed in connection with the coefficient of friction.

The deformations induced in that part of the tread in contact with the supporting surface were examined by the method of Holt and Cook (*Bureau of Standards, Journal of Research*, 1, No. 1, July, 1928), but the results—illustrated by figures in the original paper—were not easy to interpret; the most noticeable effect of the applied force was a tendency to close up the hollows in the tread pattern.

The foregoing results show that rubber, on account of its great deformability, is an exception to the ordinary laws of mechanics in that the coefficient of friction between it and other materials is not determined solely by the nature of the contacting surfaces.

### 7. Static Friction and Dynamic Friction

So far only the static friction (*i. e.*, friction which must be overcome to *initiate* motion) has been dealt with. The dynamic friction between surfaces already in relative motion and the dependence of this friction on the velocity are, however matters of great practical importance.

For slightly deformable materials the dynamic friction is less than the static friction, and the former decreases with increasing velocity. The following results (taken from *Bulletin 67* of the Engineering Experiment Station, Iowa State College, "Tractive Resistance and Related Characteristics of Roadway Surfaces," by T. R. Agg) show that the first of these conclusions applies also to rubber tires; except where otherwise stated, the dynamic friction was determined at 3 to 5 miles per hour (see Table X).

TABLE X

| Surface | Tire | Load on Axle, Lbs. | Static Friction $f$ | Dynamic Friction $f$ |
|---|---|---|---|---|
| | Pneumatics | | | |
| Portland cement, dry | Goodrich 36 × 6 | 2700 | 0.687 | 0.609 |
| Portland cement, dry | Goodrich 36 × 6 | 3200 | 0.676 | 0.590 |
| Portland cement, wet | Goodrich 36 × 6 | 2700 | 0.565 | 0.517 |
| Portland cement, dry | Blackhawk 33 × 4* | 1470 | 0.854 | 0.775 |
| Portland cement, dry | Blackhawk 33 × 4* | 1940 | 0.783 | 0.739 |
| Portland cement, wet | Blackhawk 33 × 4* | 1470 | 0.627 | 0.547 |
| Portland cement, wet | Blackhawk 33 × 4* | 1940 | ... | 0.627 |

TABLE X (*Continued*)

| Surface | Tire | Load on Axle, Lbs. | Static Friction $f$ | Dynamic Friction $f$ |
|---|---|---|---|---|
| Wood blocks, dry | Goodrich 36 × 6 | 2700 | 0.673 | 0.536 |
| Wood blocks, dry | Goodrich 36 × 6 | 3270 | 0.602 | 0.537 |
| Wood blocks, wet | Goodrich 36 × 6 | 2700 | 0.395 | 0.273 |
| Wood blocks, dry | Blackhawk 33 × 4 | 1470 | 0.776 | 0.715 |
| Wood blocks, dry | Blackhawk 33 × 4 | 1940 | 0.697 | 0.649 |
| Wood blocks, wet | Blackhawk 33 × 4 | 1470 | 0.392 | 0.303 |
| | Solid tires† | | | |
| Portland cement, dry | U. S. 36 × 4 | 4420 | 0.600 | 0.458 |
| Portland cement, dry | U. S. 36 × 4 | 3560 | 0.599 | 0.459 |
| Portland cement, wet | U. S. 36 × 4 | 4420 | 0.349 | 0.311 |
| Portland cement, dry | U. S. 36 × 6 | 4630 | 0.625 | 0.533 |
| Portland cement, dry | U. S. 36 × 6 | 3640 | 0.691 | 0.566 |
| Portland cement, wet | U. S. 36 × 6 | 4630 | 0.488 | 0.408 |
| Wood blocks, dry | U. S. 36 × 4 | 4420 | 0.571 | 0.467 |
| Wood blocks, dry | U. S. 36 × 4 | 3560 | 0.595 | 0.471 |
| Wood blocks, wet | U. S. 36 × 4 | 4440 | 0.238 | 0.225 |
| Wood blocks, dry | U. S. 36 × 6 | 4630 | 0.580 | 0.506 |
| Wood blocks, dry | U. S. 36 × 6 | 5830 | 0.557 | 0.506 |
| Wood blocks, dry | U. S. 36 × 6 | 3640 | 0.595 | 0.531 |
| Wood blocks, wet | U. S. 36 × 6 | 4630 | 0.299 | 0.250 |

* Dynamic friction determined at 10 to 12 miles per hour.
† These tires had been used and the treads worn smooth.

The coefficient of friction is not greatly influenced by varying the load, and there is no systematic difference between pneumatics and solids, but the type of road surface is important. (It may be added that ice lowers the coefficient of friction by 0.2 or 0.3.)

Braking tests on an omnibus travelling at 12 miles per hour (cf. *Le Poid Lourds*, Dec. 15, 1927, 43) showed that the coefficients of dynamic friction on stone, wood, and asphalt were about the same when the surfaces were dry, but decreased in the order named when the surfaces were wet or greasy, and were always much lower on the wet than on the dry surface. With a given braking force a greater distance was required to bring the vehicle to rest on pneumatic tires than on solid tires, especially when the tires were worn.

Agg (*loc. cit.*) gives the following values for the coefficient of dynamic friction perpendicular to the plane of the wheel: Federal and Royal Cord 33 × 4 pneumatics: $f_n^I = 0.387$; solid tire (badly worn): $f_n = 0.324$. These values seem unexpectedly low.

## Summary

(i) The coefficients of friction ($f^I$ and $f_n^I$) of rubber tires on dry non-dusty surfaces are practically independent of the load on the wheel, and (with pneumatics) of the inflation pressure; on muddy surfaces the coefficients (especially $f_n^I$) tend to decrease with increasing load.

(ii) Dust, mud, or water reduces the friction with rubber tires, but not with iron tires.

(iii) The tread pattern reduces the friction on dry surfaces, but increases it on muddy surfaces.

(iv) There is no systematic difference between pneumatic, semi-pneumatic (cushion) and solid tires as regards coefficient of friction; the details of individual design and material are the deciding factors; this is in agreement with the results of Bredtscheiner (*Verkehrstechnik*, **1922**; see Schaar, "Die Beanspruchung der Strassen durch die Kraftfahrzeuge," Zementverlag, 1925).

(v) There is no simple relationship between the coefficient of friction and the compressibility or area of contact of the tire.

(vi) The static friction perpendicular to the direction of travel is greater than in this direction.

(vii) The coefficient of friction depends on the type of road surface, its deformability, and especially on the presence or absence of dust, mud, or water.

(viii) Rubber tires have a much higher coefficient of friction than iron tires, especially on dry hard surfaces.

(ix) The static friction is 10 to 20 per cent higher than the dynamic friction.

[Reprinted from Industrial and Engineering Chemistry
Vol. 21, No. 9, page 872. September, 1929.]

# Transformation of Energy by Rubber[1]

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**Energy expended on raw or vulcanized rubber is consumed largely by producing plastic flow and reversible elastic strain. The most rapid energy transfer is the most completely reversible since the plastic flow is reduced. Stress-strain curves obtained rapidly become straight lines through elimination of plastic flow, and the curves obtained at the higher temperature show the greatest load-carrying capacity. Rebound increases with the temperature, but is not greatly affected by vulcanization. The physical changes produced by vulcanization seem to be caused largely by suppression of plastic properties rather than by the creation of elastic material.**

IT HAS long been known that a strain produced suddenly in a strip of rubber is accompanied by a rise in temperature. Conversely, when the strain is quickly released heat is absorbed, with a resulting decrease in temperature of the strip, or if the retraction is very slow the temperature will remain constant and heat energy will be drawn from the surrounding atmosphere. In these changes rubber is only the medium for the transformation of energy. Besides being converted into heat, mechanical energy may be transformed into many other types, such as electrical energy and surface energy. Some of these, such as electrical energy, can be detected, while others, such as surface energy, are suspected of playing some part in the phenomena attending the strain of a piece of rubber. Heat energy, regardless of the mechanism of its origin within the rubber, is the predominating type of energy produced by stretching, and since

[1] Presented before the Division of Rubber Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

it is largely reversible a close relationship should exist between heat energy produced or absorbed and mechanical energy expended or consumed.

### Heat and Mechanical Energy in Vulcanized Rubber

The approximate amount of heat liberated upon stretching a strip of rubber has been determined by measuring the temperature rise. The temperature rise, specific heat, and specific gravity permit the calculation of the amount of heat energy liberated. Mechanical means were supplied for stretching the strip to the desired elongation in about 1 second. A strip of rubber 10 cm. by 1 cm. by 3 mm. was stretched inside a long glass tube loosely closed at each end with cotton. This precaution was necessary because of the effect of air currents on the temperature of the strip. A calibrated thermocouple, the junction of which was composed of No. 40 B. and S. gage copper and constantan wire reduced to half this diameter at the tip, was threaded into the side of the rubber strip so that the junction was approximately at the center. After the strip had assumed a uniform temperature, it was stretched and the temperature rise was determined from the deflection produced in a suspension galvanometer. The maximum deflection was obtained in about 5 seconds and the cooling curve was followed every 5 seconds for 1 minute. The temperature rise was then obtained by extending the cooling curve back to 1 second. The temperature rise obtained in this way was about 4 per cent higher than that indicated by the maximum deflection. Measurements of the heat generated at various elongations were all made on the same strip of rubber. The temperature rise after a complete rapid extension and retraction at a high elongation was also determined.

Stress-strain curves were made on the same compound. Dumb-bell test pieces which had been quickly stretched five times to 60 per cent of their breaking elongation were used. The clamps of the test machine separated at the rate of 20 inches (51 cm.) per minute.

The data shown in Table I were obtained with an accelerated pure-gum type of rubber with heat capacity of 0.465 calorie per cubic centimeter per degree and specific gravity of 0.998. The heat energy and mechanical energy are both expressed in joules and in each case the figures represent the total change involved from zero elongation up to the elongation indicated.

These figures are interesting if viewed from the standpoint of efficiency of transformation of energy. The heat energy liberated upon stretching the rubber appears to be greater than the mechanical energy required to stretch the strip. This discrepancy will later be shown to be due to the fact that the rapid stretching of the strip used for determining the temperature rise caused more work to be done on this strip than on the strip used in obtaining the stress-strain curve.

The only deduction to be made from these data is that at least a large part of the mechanical work is changed reversibly into heat energy. Viewed independently, the heat cycle shows an efficiency of 94.2 per cent as measured by the heat liberated at 600 per cent elongation and the heat remaining after a complete cycle, while the mechanical cycle as measured from stress-strain data shows an efficiency of only 85.6 per cent.

**Table I—Heat Energy and Mechanical Energy in a Strip of Vulcanized Rubber**

| Elongation | From Temperature Rise | | From Stress-Strain | |
|---|---|---|---|---|
| | Temperature rise | Heat energy | Mechanical energy for extension | Mechanical energy for retraction |
| *Per cent* | *° C.* | *Joules* | *Joules* | *Joules* |
| 200 | 0.332 | 0.479 | 1.005 | 0.400 |
| 300 | 0.674 | 1.310 | 1.980 | 1.040 |
| 400 | 1.052 | 2.050 | 3.270 | 2.070 |
| 500 | 2.340 | 4.550 | 5.050 | 3.830 |
| 600 | 4.230 | 8.230 | 7.770 | 6.640 |

Residual heat after a complete cycle to 600 per cent elongation was 0.48 joule.

### Mechanical Work as Temperature of Rubber Is Varied

Since the above comparison was rather unsatisfactory, an attempt was made to measure the mechanical work done when the temperature of a strained strip of rubber was changed. An agitated electrically heated bath filled with either water or ethylene glycol was used to control the temperature of the rubber. The test piece was in the form of a ring having a cross section of about 2 sq. mm. The rubber was stretched between two hooks, one being fastened in the bottom of the bath and the other leading to one arm of a balance directly above. The load was applied to the other arm of the balance and the elongation was followed by means of a pointer attached to one of the balance arms. In conducting the test, the bath temperature was adjusted to 25° C. and the strip was strained to the desired initial elongation by loading one side of the balance. The temperature was then raised at the rate of 25° C. per minute and the corresponding temperature and elongation were recorded.

The data obtained by this method are of little value for determining quantitatively the transformation of heat into mechanical energy. In some cases the elongation increased continually as heat was applied and work was actually done on the rubber. In other cases a material decrease in length was noted, but the work done by the rubber represented only a small part of the heat absorbed by the rubber.

The data shown in Table II were obtained with a compound composed of 100 parts of rubber and 10 parts of sulfur, which was cured on a mandrel in open steam at 148° C.

The data presented in Table II confirm the observation made by van Rossem and van der Meijden (*4*) that vulcanized rubber exhibits plastic properties. They also show the tendency of rubber in the higher states of vulcanization to

break at a low elongation when stretched at a high temperature, as has been shown by Somerville (*3*). These data also show the ability of strained rubber to convert heat into mechanical energy. The test conducted on the 30-minute cure at 400 per cent elongation clearly shows the Joule effect. The shortening of the strip and the lifting of the load continue until the temperature has reached 70° C., when the plastic flow of the rubber has become great enough to more than balance the shortening of the strip due to the Joule effect. As the temperature is increased the plastic flow increases, causing the strip to elongate, and part of this elongation remains as a permanent set of 38 per cent after the test is completed and the load removed from the rubber. When the test is started at an initial elongation of 500 per cent, the load is great enough to cause rapid plastic flow from the beginning and the Joule effect is entirely masked. When the cure is increased to 60 minutes, the Joule effect is shown at all initial elongations although only to a slight extent at the highest elongation where the rubber is under the greatest load. All the tests except the 90-minute cures show flow of the rubber at the high temperatures. The more vulcanized strips broke before a temperature high enough to cause this flow was reached. In general, the temperature at which the plastic flow masks the Joule effect for any given cure increases as the initial elongation and load decrease. The high elongations also show the inability of the rubber to withstand more than a moderately high temperature. The temperature at which stretched rubber will break will be found to decrease with increasing cure and increasing load. It will also be noticed that unvulcanized rubber shows the Joule effect, its action differing from that of a vulcanized strip only in degree.

### Effect of Initial Permanent Set

The initial permanent set in the rubber is an important factor in determining the changes which take place when the strained rubber is heated. This is true because the elimination of as much of the initial plastic flow as possible permits the Joule effect to be more easily observed. Assuming that sufficient time is allowed for the test in every case, the greatest factor influencing permanent set is force applied. Elongation is the result of the application of force and is not a direct cause of permanent set. Plastic flow requires a force greater than some definite minimum. The greater this excess the more rapid will be the plastic flow. For this reason the Joule effect is more easily masked when the greatest load and highest elongation are used.

During the initial period of stretching rubber behaves like an elastic network surrounding a dispersed plastic phase which changes from some more or less regular shape into slender rods. Once the rods are formed, tendency for further flow is very much decreased. If as much deformation of the

**Table II—Per Cent Elongation of Loaded Strips of Rubber as Temperature Is Varied**

| Temperature of Rubber | Elongation at Cure of: | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 Minutes[a] | 30 Minutes | | | 60 Minutes | | | | | 90 Minutes | |
| ° C. | % | % | % | % | % | % | % | % | % | % | % |
| 25 | 100 | 400 | 500 | 600 | 200 | 300 | 400 | 500 | 600 | 300 | 400 |
| 30 | 99 | 398 | 500 | 600 | 198 | 295 | 399 | 499 | 600 | 299 | 397 |
| 35 | 96 | 395 | 500 | 605 | 192 | 291 | 395 | 497 | 598 | 297 | 394 |
| 40 | 96 | 392 | 502 | 610 | 190 | 288 | 391 | 495 | 597 | 296 | 393 |
| 45 | 98 | 388 | 506 | 615 | 187 | 286 | 388 | 494 | 597 | 295 | 392[b] |
| 50 | 101 | 385 | 512 | 630 | 185 | 284 | 385 | 494 | 597 | 295 | |
| 60 | 115 | 384 | 527 | 645 | 183 | 281 | 381 | 494 | 597 | 294[b] | |
| 70 | 123 | 382 | 545 | 665 | 182 | 278 | 379 | 495 | 599 | | |
| 75 | | 383 | 553 | | 181 | 277 | 378 | 497 | 600 | | |
| 80 | | 384 | 562 | | 181 | 277 | 378 | 498 | 603[b] | | |
| 90 | | 386 | 574 | | 180 | 276 | 379[b] | 503[b] | | | |
| 100 | | 387 | 582 | | 179 | 278 | | | | | |
| 110 | | 388 | 588 | | 180 | 281 | | | | | |
| 120 | | 392 | 600 | | 184 | 289 | | | | | |
| 130 | | 405 | | | 191 | 302 | | | | | |
| 140 | | | | | 207 | 326 | | | | | |
| Per cent set at end of test | | 38 | 90 | 47 | 18 | 23 | 10 | 15 | 15 | 5 | 5 |

[a] Obtained with a piece of unmilled smoked sheet rubber.
[b] Indicates strip broke at that temperature.

plastic portion as possible is obtained before heat is applied, shortening of the strip will be very much more pronounced. When the temperature of the rubber is raised high enough, the strip will again begin to elongate. This flow definitely affects the elastic portion of the rubber, but it cannot be true plastic flow since it seems to be limited in amount. A permanent set of 100 per cent is often found, but very rarely will 200 per cent be reached.

**Table III—Effect of Initial Permanent Set on Change in Elongation of a Stretched Rubber Band When Heated**

| Temperature | Elongation on Curing at 140° C. | | | | | |
|---|---|---|---|---|---|---|
| | 15 Minutes | | | | 20 Minutes | |
| | Original Permanent Set | | | | | |
| | 0% | 8% | 0% | 10% | 0% | 8% |
| ° C. | % | % | % | % | % | % |
| 25 | 200 | 200 | 500 | 500 | 300 | 300 |
| 30 | 197 | 193 | 500 | 499 | 300 | 297 |
| 35 | 195 | 188 | 500 | 498 | 298 | 294 |
| 40 | 192 | 187 | 500 | 496 | 295 | 289 |
| 50 | 190 | 182 | 503 | 495 | 292 | 282 |
| 60 | 188 | 176 | 513 | 491 | 290 | 275 |
| 70 | 188 | 172 | 528 | 483 | 288 | 268 |
| 80 | 190 | 168 | 546 | 480 | 288 | 262 |
| 90 | 194 | 164 | 566 | 486 | 289 | 258 |
| 100 | 201 | 162 | 589 | 506 | 292 | 261 |
| 105 | 205 | 163 | | | 296 | 265 |
| 110 | 210 | 165 | | | 304 | 272 |
| 115 | 215 | 169 | | | 315 | 279 |
| 120 | 224 | 176 | | | 332 | 291 |

The data in Table III were obtained with a stock composed of 100 parts of smoked sheet, 5 parts of zinc oxide, 3 parts of sulfur, and 1 part of butyraldehyde aniline accelerator and illustrates the effect of the initial plastic flow on the action of the strained rubber when it is heated.

The introduction of the idea of plastic flow requires the consideration of the element of time. A strip of rubber may be stretched quickly with little resulting permanent set, but by holding in a strained condition for a period of time considerable permanent elongation will result. Plastic flow of any portion distributed through the elastic network will be caused by slow stretching and will be reversed when the strain in the rubber is released due to energy which is stored in the rubber. The speed of the flow in the reverse direction becomes slower as the force exerted by the rubber becomes less and, since plastic flow requires a force beyond a definite minimum, the flow will cease when the force in the rubber has reached this minimum. The remaining deformation in the strip will remain as permanent set. This set can be somewhat further reduced by warming the strip which increases the plasticity of the plastic portion and the force resulting from the remaining strain in the vulcanized network.

### Stress-Strain Curves

Since all the tests which we apply to rubber involve a greater or less extent of time, it follows that all the results are

a composite of elastic strain and plastic flow. This is especially true of such tests as the determination of stress-strain curves, which occupy considerable time. As shown recently by the Physical Testing Committee of the Division of Rubber Chemistry of the American Chemical Society (*2*), stress-strain curves obtained at a high temperature show a lower load-carrying capacity than those obtained at a lower temperature. This is especially true of compounds to which certain softeners and plastic material have been added. Since a strained strip of rubber exerts a greater force when heated, a softer stress-strain curve can be obtained only when the plastic flow overcomes the Joule effect.

It is possible to overcome the plastic flow to a large extent by conducting the test in as short a time as possible and when stress-strain curves are obtained in 2 or 3 seconds a greater

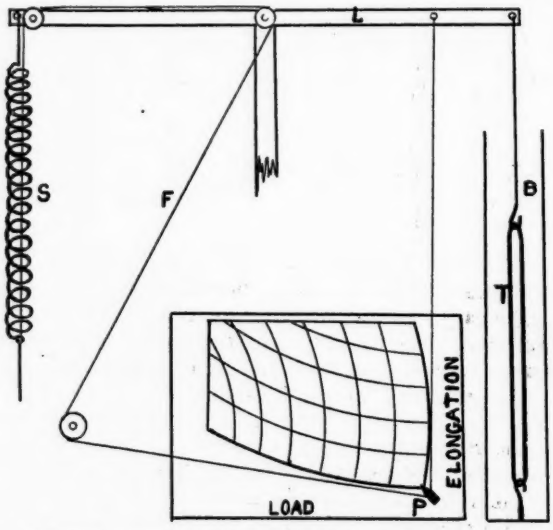


**Figure 1—Apparatus for Plotting Stress-Strain Curves**

load-carrying capacity is shown at a higher temperature. This is especially true if part of the initial plastic flow is eliminated by stretching the rubber a few times before conducting the test.

A simple apparatus for plotting stress-strain curves is shown diagrammatically in Figure 1. The test strip, *T*, which is in the form of a ring, is fastened to one end of the lever arm, *L*, and to the bottom of the bath, *B*. The bath is filled with water or ethylene glycol and can be held at any temperature. Force is applied to the strip by means of the spring, *S*, which is attached to the other end of the lever arm. Elongation of the strip is recorded by the pen, *P*, which is attached to the test-piece side of the lever arm. The force exerted is recorded through the thread, *F*, which passes

from the pen, over pulleys at the fulcrum, and at the spring end of the lever, and is attached to the bottom of the spring.

Figure 2 is a chart obtained with an apparatus of the type just described when using an accelerated pure-gum type of compound which was vulcanized to a point considerably below the maximum attainable physical strength. The ring test piece was stretched several times previous to conducting the test in order to remove at least part of the permanent set, which if permitted to remain would tend to make the second stress-strain curve fall too low on the load axis because the initial length of the test ring would be increased. The curves were carried only to a relatively low elongation in order that the load imposed would not be great enough to cause plastic flow, which would appear as set and interfere with the next test. After the test ring had been slowly stretched several times to 600 per cent elongation, its circumference was measured. This was necessary in order to permit construction of the proper elongation spacings for the chart on which the curves were recorded. The test ring was then placed in the machine and the curves were obtained as rapidly as the bath could be raised from one temperature to another without removing the test ring between tests.

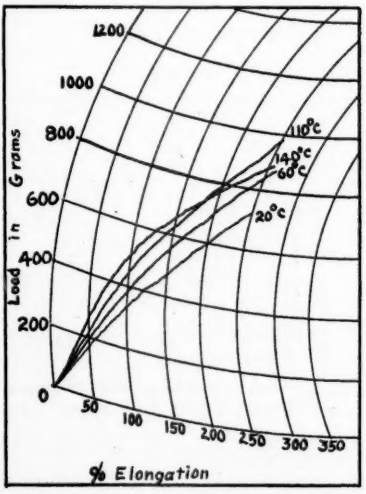


**Figure 2—Stress-Strain Chart Obtained with Apparatus Shown in Figure 1**

The curves obtained are what could have been predicted from the experiments previously described. In each case an increase in temperature has resulted in a greater load-carrying capacity for the rubber. In addition to greater load-carrying capacity, the curve obtained at 140° C. also shows plastic flow. In this case the load has increased and the temperature has been raised until a yield point has been reached. This same phenomenon can take place at a lower temperature if the elongation is increased.

These curves have been transposed to rectangular coordinates in Figure 3 and the stress-strain curve calculated from data obtained at 20° C. with a dumb-bell test strip in the usual manner is added for comparison. It will be seen that the curves obtained at a rapid rate are practically straight lines, which indicates that the elastic portion of rubber obeys

Hooke's law. This is true as long as no flow takes place. In the curve obtained at 140° C. the stress-strain relationship of the elastic rubber is partly masked by flow at the higher elongations. All ordinary stress-strain curves show the effect of plastic flow at low elongations, but when higher elongations are reached the curves straighten out and the change in stress becomes nearly proportional to change in strain. The slope of this portion of the curve has been used by De Vries as an index to the quality of the rubber. The displacement of this part of the curve to the right or left would indicate roughly the amount of plastic material. The curves obtained at the rapid rate at both 20° and 60° C. are entirely reversible, while the retraction curve obtained by the ordinary slow method shows an initial rapid decrease in the load due to the fact that the energy stored in the strip is being consumed to cause the rapid reversal of flow of the plastic portion.

It is interesting to note in any series of stress-strain curves obtained with different periods of vulcanization of the same stock that at high elongation the curves are parallel. After most of the plastic flow is eliminated elastic strain becomes the dominant factor and the strain produced by unit stress is constant over a wide range of cures. This condition exists until continued vulcanization appears to destroy part of the elastic properties when the strain produced by unit stress becomes greater. Plastic deformation shown by the first part of the curve decreases as the vulcanization period is lengthened until an overcured condition is reached. These facts indicate that the greatest effect of vulcanization is a change in the plastic properties of the rubber and that the elastic properties change very little. Whether the plastic and elastic properties are contained in the same or in different molecules need not be considered. In any case the elastic properties are shown by rubber which has had only a very short period of vulcanization, and by suppressing the plastic properties it should be possible to demonstrate the elastic properties of unvulcanized rubber. The requirement of such a test is the elimination as far as possible of the time factor, since time is required for plastic flow.

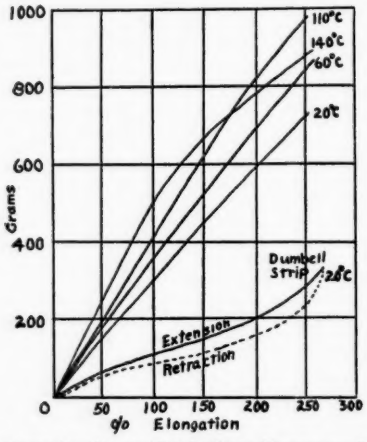


**Figure 3—Stress-Strain Data Transposed to Rectangular Coördinates**

## Rebound

Rebound is a very simple test which can be applied to rubber and which eliminates the time factor to a certain extent. When a rigid weight is dropped on a piece of rubber, all the kinetic energy of the weight is transferred to the rubber. Since the rubber is elastic, potential energy is stored in the rubber and is returned to the weight, but part of the original energy is lost during the transfer. Lubricating the contact between weight and rubber does not increase the rebound, which shows that the energy loss is in the rubber and not between the surfaces of weight and rubber. This loss of energy is due to internal frictional resistance caused by motion of the rubber, and since the time factor is not entirely eliminated part of the loss is due to plastic flow. Rebound should then be increased by any factors which would tend to reduce the amount of motion and to decrease the resistance to plastic flow. These conditions are filled by an increase in temperature, which increases plasticity and at the same time gives the rubber the ability to support a greater load at a given elongation, which means that the motion is reduced. The data given in Table IV show the increase in rebound with temperature for both raw and cured samples of the same pure-gum type rubber compound.

**Table IV—Effect of Temperature and Vulcanization on Rebound**

| Temperature | Rebound | |
|---|---|---|
| | Uncured | Cured |
| ° *C.* | *Per cent* | *Per cent* |
| 15 | 59 | 63 |
| 23 | 63 | 67 |
| 50 | 72 | 76 |
| 70 | 78 | 81 |
| 90 | 79 | 85 |

These figures show the elastic property of unvulcanized rubber and also indicate that the temperature of unvulcanized rubber can be increased to a point where rebound no longer continues to increase. This point may correspond to the high-temperature flow observed in vulcanized rubber. Any study of the elastic properties of crude rubber by the rebound method should then be made at room temperature. It is also apparent that the change brought about by vulcanization has produced only a slight increase in rebound. This could be caused by either a decrease in plastic properties or an increase in elastic properties or both.

The suggestion is contained in both the series of stress-strain curves and in rebound figures that vulcanization consists essentially in suppressing the plastic properties of the rubber and not in creating elastic properties. If this is true, the rebound value of raw rubber should serve as a rough index to its quality. Since rebound is still a composite of elastic and plastic properties, and does not distinguish between quality and quantity of either elastic or plastic material,

the test cannot be expected to be extremely accurate, but should roughly classify crude rubber into different grades.

In the determination of rebound it is essential that uniform conditions be followed. To support the uncured rubber, metal rings 1 cm. thick and 3 cm. in diameter were used. The rubber was pressed into these rings and permitted to adhere to a heavy metal base plate. The top of the rubber was covered lightly with soapstone and a smooth weight was placed on the slightly warmed rubber until a smooth surface was obtained. The steel weight used in the rebound test was 7 cm. long and 2 mm. in diameter. The ends of the weight were rounded. This was dropped through a glass guide tube from a height of 50 cm. It is essential that the guide tube be exactly perpendicular and not touch the surface of the rubber.

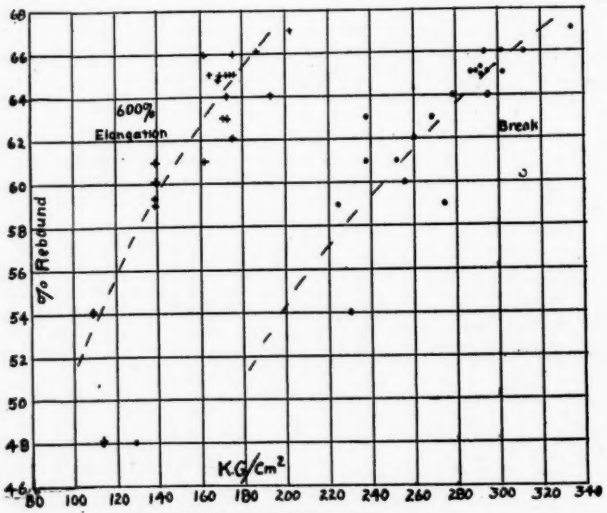


**Figure 4—Rebound Data**

A number of different samples of rubber have been examined for rebound before vulcanization and physical properties after vulcanization. Unless stated otherwise, all samples were milled on a very hot mill in order to preserve the original state as far as possible. The compound used was 100 parts of rubber, 5 parts of zinc oxide, 3 parts of sulfur, and 1 part of di-*o*-tolylguanidine. Vulcanization was carried out at 140° C. Maximum tensile and stress at 600 per cent elongation were taken from curves plotted to show changes of these properties with time of cure. Results are shown in Table V.

These data are plotted in Figure 4. While the points do not fall on a smooth curve, the tendency for decreased tensile and load-carrying capacity to accompany decreased rebound is shown. For rebound above 60 per cent the increase in tensile is very roughly 7 kg. per square centimeter for each

per cent increase in rebound. The curves cannot be straight lines, since they do not incline toward the origin through which they must pass.

**Table V—Rebound of Unvulcanized Rubber and Physical Properties after Vulcanization**

| Type of Rubber | Rebound at 24° C. | Max. Load at 600% Elongation | Max. Tensile |
|---|---|---|---|
| | *Per cent* | *Kg./sq. cm.* | *Kg./sq. cm.* |
| Smoked sheets | 64 | 194 | 296 |
| Smoked sheets, gassy | 63 | 172 | 268 |
| Smoked sheets, moldy | 62 | 175 | 260 |
| Smoked sheets, clean, ribbed | 66 | 176 | 311 |
| Smoked sheets, clean | 66 | 188 | 302 |
| Smoked sheets, clean | 65 | 175 | 290 |
| Smoked sheets, clean | 65 | 163 | 290 |
| Smoked sheets, clean | 65 | 170 | 295 |
| Pale crepe | 66 | 161 | 294 |
| Pale crepe | 65 | 173 | 288 |
| Para ham, washed | 67 | 203 | 336 |
| No. 1 amber blanket | 61 | 140 | 252 |
| No. 1 amber blanket | 65 | 170 | 292 |
| No. 1 amber blanket | 64 | 173 | 279 |
| No. 1 amber blanket | 65 | 177 | 303 |
| No. 2 amber blanket | 60 | 140 | 246 |
| No. 2 amber blanket | 63 | 172 | 238 |
| No. 3 amber blanket | 59 | 140 | 276 |
| Roll brown | 54 | 111 | 131 |
| Roll brown | 59 | 140 | 224 |
| Smoked sheets, milled cold 40 min. | 48 | 115 | 130 |
| Sheets 85, mineral rubber 10, pine tar 5 | 61 | 161 | 238 |

It is true in general that in any given series of polymers the smaller molecules are more reactive chemically. Since vulcanization involves a chemical combination of sulfur, the rubber having the largest proportion of the smallest molecules should combine with sulfur at the greatest rate. While milling will greatly increase the plasticity of rubber, this increase should be at the expense of the elastic network and of the largest aggregates more than of the aggregates of medium size. In spite of the fact that the number of the smallest aggregates may not be greatly increased by milling, the rate of combination of sulfur seems to be slightly increased. A sample of rubber milled with 10 per cent of its weight of sulfur for 40 minutes on cold rolls had combined 1.86 per cent of sulfur after $2^1/_2$ hours' cure at 140° C. A similar mixture produced in a short time on hot rolls combined only 1.72 per cent of sulfur. This indicates that an increase of 8 per cent in the rate of combination has been caused by milling, although the physical state of the excessively milled rubber would indicate that no cure had taken place. Axelrod (*1*) showed a similar increase after the rubber was plasticized by heat.

## Conclusion

The data which have been presented indicate that elasticity is a property of rubber which persists through vulcanization and is not created to any great extent. The physical state of the rubber after any period of cure depends on the balance between suppression of plastic properties

either directly or indirectly through the influence of combination of sulfur, and the creation of plastic properties through the influence of heat. It is probable that sulfur also combines at a slower rate with the elastic portion of the rubber and finally results in a product of almost no mechanical strength.

The transformation of energy by rubber depends upon the condition of the rubber as well as on the condition of the test. Heat liberated by elastic strain can be transformed almost quantitatively into mechanical work. Heat due to internal-frictional resistance which will be caused by both plastic and elastic flow is not reversible. Any reduction in time required for the transfer of energy reduces the amount lost through plastic flow. An increase in temperature increases the resistance of the elastic portion to strain, but also reduces the resistance to flow of the plastic portion. Sufficient increase in temperature causes a large energy loss due to a considerable but limited permanent flow of the rubber. This cannot be plastic flow of the elastic portion, since it is limited in extent, but can better be explained by some mechanical change such as a breaking of the anchorage between portions of the plastic material and elastic network.

## Literature Cited

(1) Axelrod, *Gummi-Ztg.*, **24**, 352 (1909).
(2) Partenheimer, IND. ENG. CHEM., **20**, 1245 (1928).
(3) Somerville, *Rubber Chem. Tech.*, **2**, 1 (1929).
(4) Van Rossem and van der Meijden, *Ibid.*, **1**, 393 (1928).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1027. November, 1929.]

# Influence of Pigments on Some Physical Properties of Unvulcanized Rubber[1]

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**The solubility of pigmented rubber in benzene can be changed by altering the interfacial energy between the rubber and the pigment, and this can be accomplished either by changing the surface of the pigment or by changing the nature of the rubber—as, for example, by treating zinc oxide with sulfur trioxide gas and by adding organic acid to rubber.**

**A plausible explanation has been offered as to why pigments cause rubber to become insoluble. In specific cases it has been possible to predict the solubility of unvulcanized rubber containing pigments.**

**Data are presented showing the change in solubility of unvulcanized rubber during storage in contrast to the constancy in consistency, which gives evidence of a weak rubber structure that develops in storage.**

**The influence of time and temperature of milling on consistency and solubility is shown.**

IT IS generally known that unvulcanized rubber compounds containing fine pigments dissolve or, as some technologists prefer to say, disperse, slowly in solvents such as benzene.

*Note*—For the sake of clarity, the term "solubility" has been used in this paper to denote the dispersion of the rubber compound in the solvent and the term "dispersion" has been used in discussing the distribution of pigment in the rubber.

The compounds are not really insoluble, as shown by the

[1] Presented before the Division of Rubber Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

fact that fine pigment added to a rubber cement does not precipitate the cement; they are just difficult to disperse. Beakers *A* and *C* in Figure 1, containing carbon black and a fine-particle-size zinc oxide, respectively, illustrate the insolubility. The stock compounded with an ordinary zinc oxide shown in beaker *B* is dissolving much more rapidly.

*Note*—In this report the fine particle-size zinc oxide has a particle size of 0.15 micron and is known by the brand name, Kadox. The ordinary zinc oxide has a particle size of about 0.30 micron and is known as XX Red.

If this were all of the story, the rate of solution would give a qualitative method of grading pigments within a certain range of particle size, but factors other than particle size influence the solubility. When stearic acid is added to the compounds, the solubility of the stock containing the fine-particle-size zinc oxide is greatly increased, as shown in beaker CI, whereas the carbon black stock, shown in AI, remains insoluble.

### Theory of Insolubility of Pigmented Rubber

One explanation of the insolubility is that the pigments are in a flocculated state in the unvulcanized rubber and the flocculent structure acts as a semi-permeable membrane which prevents the rubber aggregates from passing through. The common rubber solvents are known to be strong flocculating agents for pigments and they would tend to keep the pigment in its flocculated state. The flocculated pigment particles, each surrounded by rubber except at the point of contact, make threads and sheets which run irregularly throughout the compound and inter-mesh in every direction making a network of pigment, so that it would be conceivable for an electron, as an example, to move from any part of the compound to any other part along the chain of pigment particles without leaving pigment.

The addition of stearic acid (beakers AI, BI, and CI) disperses the zinc oxide—*i. e.*, breaks down the flocculated pigment structure—and thereby destroys the semi-permeable membrane and increases the solubility. The very considerable increase in softness due to the addition of the stearic acid is in itself impressive evidence that a flocculated structure has been destroyed.

When a pigment is spoken of as dispersed or flocculated, it does not mean that all the particles are dispersed or all flocculated. It is quite likely that in every mix containing pigments there are aggregates, unmixed pigment, dispersed pigment, and flocculates. The expression "flocculated" means that a large enough percentage of the particles is in this state to give the rubber properties, such as stiffness and insolubility, that are characteristic of flocculated pigment.

When pigments are milled into rubber, they are usually incorporated in small groups; then the mixing action breaks up the groups of pigment particles and coats the individual particles with rubber. If the wetting of the pigment by the rubber

is poor, the individual particles will stick together when they come into contact, and they will then be spoken of as flocculated. A considerable amount of dispersion and flocculation takes place when the rubber is hot and fluid during the early stages (*3*, *4*) of vulcanization.

It is generally recognized that a quantitative relationship cannot be developed between the size of the opening in a semi-permeable membrane and the size of particle that will diffuse through it, but it seems reasonable that there should be at least an order-of-magnitude relationship in the case of pigmented unvulcanized rubber. Three flocculated spherical pigment particles, 0.3 micron in diameter, will form an

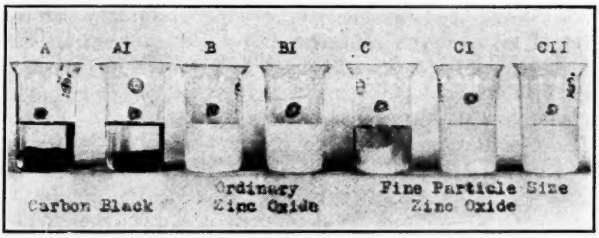



**Figure 1—Influence of Particle Size and Interfacial Tension on the Solubility of Rubber Stocks Containing Pigments**

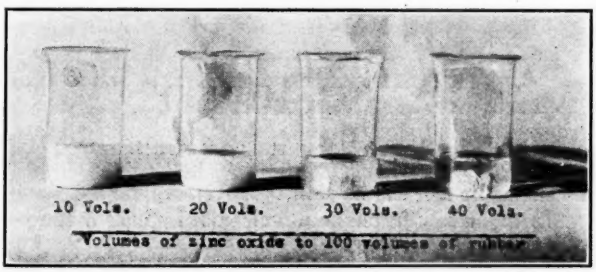



**Figure 2—Influence of Pigment Concentration on Solubility of Unvulcanized Rubber**

Photograph taken 2½ hours after immersion of rubber in benzene

opening that will allow a sphere 470 Å. to pass through, according to F. A. Steele of this company. This is the approximate opening in an ordinary zinc oxide membrane, and published figures (*5*) for the size of the rubber micelle (300–600 × 100–200 Å.) are of the same approximate size.

Many of the openings are larger and allow rubber micelles to diffuse (*2*) through without difficulty. As they pass into the solvent the network probably draws together, owing to flocculating forces, and holds the remainder of the rubber even more tightly. This slow diffusion of unpigmented rubber through the larger openings in a semi-permeable membrane formed by a strongly flocculated pigment is to

be expected. In the case of a weakly flocculated pigment such as ordinary zinc oxide, the flocculated structure is sufficient only to delay solution, and the experiments described in this paper refer to the relative solubilities over very short periods of time.

It might be thought that the increased rate of solution and the decreased hardness are due to action of the stearic acid on the rubber rather than to change in the interfacial tension. However, there is another way to change the interfacial tension between pigment and rubber—by changing the composition of the surface of the pigment particle. This method, which should influence only the interfacial tension, was carried out by exposing the zinc oxide to the action of dilute sulfur trioxide gas and thereby forming a surface layer of zinc sulfate. Beaker CII in Figure 1 shows that rubber containing this acid-treated fine oxide is more soluble than that containing the untreated fine oxide. The unvulcanized stock is also much softer.

If the picture of the semi-permeable membrane is correct, there are two methods of testing it: first, by reducing the size of the opening in it through increasing the number of pigment particles—i. e., increasing the concentration of pigment—and second, by reducing the size of the rubber aggregates, as by severe milling.

It is well known among rubber technologists that these two criteria will agree with the theory and the data are presented for completeness in the case of pigment loading and because the time and temperature during the milling have been accurately determined, making the data in the second case quantitative.

### Influence of Pigment Concentration

From Figure 2 it will be seen that even ordinary zinc oxide produces relatively insoluble unvulcanized stocks if the pigment concentration is high enough.

### Effect of Milling

In order to study the effect of breaking down the rubber aggregates, four conditions of milling were investigated using a stock containing 100 volumes of rubber and 30 volumes of ordinary zinc oxide: (1) 15 minutes with the stock at 100° C.; (2) 60 minutes at 100° C.; (3) 15 minutes at 60° C.; (4) 60 minutes at 60° C. The temperature control during milling was made possible by means of the contact resistance thermometer described by Ashman and Homewood (*1*).

The pieces of rubber shown in Figures 3 and 4, after 10 and 20 minutes in the solvent, respectively, demonstrate that a relatively high temperature and a short milling time, which does the least work on the compound, produced the most insoluble stock and that the reverse conditions resulted

in the most soluble. From Table I it is evident that time of milling affects the solubility, as compared with consistency, to a relatively greater degree than temperature of milling.

**Table I—Consistency and Solubility Data Showing Effect of Milling**

| Conditions of Milling | | Thickness after 3 Min. in Williams Press at 70° C. | Recovery in 1 Min. after Removal from Oven[a] | Time Required for Soln. to Become Milky[a] |
|---|---|---|---|---|
| *Min.* | *° C.* | *Mm.* | *Per cent* | *Minutes* |
| 15 | 100 | 4.09 | 15.40 | 60 |
| 60 | 100 | 2.51 | 6.97 | 7 |
| 15 | 60 | 2.53 | 7.51 | 15 |
| 60 | 60 | 1.95 | 3.08 | 6 |

[a] Determined at room temperature 75° ± 5° F. (24° ± 3° C.).

It must be admitted that milling should not only break down the rubber aggregates, but should also improve the dispersion of the pigment, and hence that increased pigment dispersion is responsible for some of the increase in solubility

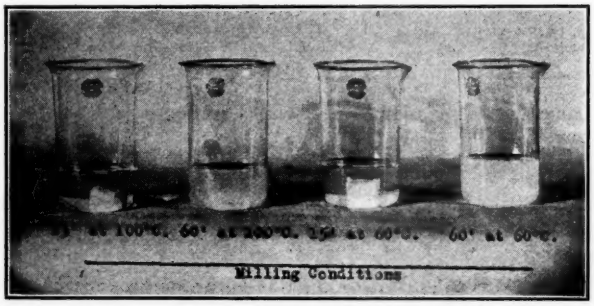



**Figure 3—Influence of Conditions of Milling of a Stock on Its Solubility**

**Photograph taken 10 minutes after immersion of rubber in benzene**

and the decrease in consistency. There is also some oxidation of the rubber, but that does not need to be considered in this paper.

It would not seem probable that the pigment dispersion could change after the stock has cooled, and this is borne out by the fact that when the milled stock is allowed to stand for months the amount of flow under the relatively heavy weight used in the Williams press (shown by the thickness after 3 minutes' compression) remains constant (Figure 5). The solubility, on the other hand, decreases sharply with time (Figure 6), which would indicate either an increase in the size of the rubber aggregates or a developing structure. This structure might be a rubber structure or it might be due to a flocculation, or precipitation, of protein particles. That this newly developed structure is weaker than the original rubber structure is shown by the fact that the flow in the press is not changed by its presence. However, the forces that determine the percentage recovery on removal from the

press are relatively small and the weak structure does affect these results somewhat, as shown by the erratic data given in Figure 7.

The data in Table II show that the flow in the press and the solubility of unpigmented rubber as determined from time to time do not change appreciably during a week's storage. The early development of a structure on storage is manifested by the changing percentage recovery on re-

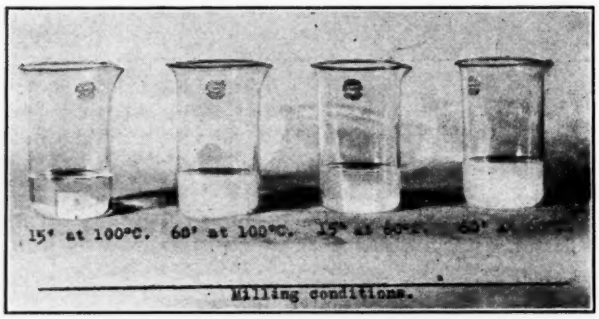



**Figure 4—Influence of Conditions of Milling of a Stock on Its Solubility**
Photograph taken 20 minutes after immersion of rubber in benzene

moval from the press; the relatively large recovery was expected since there was no pigment structure to prevent the recovery.

### Insolubility of Vulcanized Rubber

Without entering into the merits of the various theories of vulcanization, or even endorsing the ideas brought out in the brilliant paper by Stevens (*6*) to the effect that vulcanization consists in the formation of particles of hard rubber,

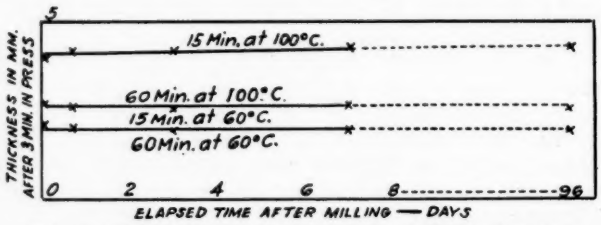



**Figure 5—Effect of Storage on Consistency of Unvulcanized Rubber That Has Been Milled under Different Conditions**

it is pertinent to point out that the concept of a flocculated structure of $C_5H_8S$ particles in vulcanized rubber would explain the insolubility of vulcanized rubber and the increase in hardness of rubber during vulcanization, without any necessity of considering special shapes and arrangements of the particles.

**Table II—Consistency and Solubility of Milled Pale Crepe**

| Conditions of Milling | | Thickness after 3 Min. in Press at 70° C. | | | | Recovery 1 Min. after Removal from Press at 75° ± 5° F. (24° ± 3° C.) | | | | Solubility—Approx. Time Required for Complete Dispersion of 1-cm. Cube at 75° ± 5° F. (24° ± 3° C.)* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time after milling | | | | Time after milling | | | | Time after milling | | | |
| | | 1 Hour | 22 Hours | 3 Days | 7 Days | 1 Hour | 22 Hours | 3 Days | 7 Days | 1 Hour | 22 Hours | 3 Days | 7 Days |
| *Min.* | *° C.* | *Mm.* | *Mm.* | *Mm.* | *Mm.* | % | % | % | % | *Hours* | *Hours* | *Hours* | *Hours* |
| 15 | 100 | 4.10 | 4.05 | 4.00 | 4.14 | 13.66 | 18.29 | 19.13 | 21.50 | 44 | 38 | 45 | 43 |
| 60 | 100 | 3.16 | 3.22 | 3.19 | 3.33 | 9.34 | 11.96 | 11.13 | 12.01 | 44 | 38 | 45 | 43 |
| 15 | 60 | 2.82 | 2.89 | 2.86 | 2.88 | 8.87 | 9.69 | 10.14 | 9.55 | 20 | 20 | 24 | 24 |
| 60 | 60 | 1.67 | 1.63 | 1.57 | 1.60 | 1.24 | 3.07 | 3.51 | 2.81 | 10 | 12½ | 16 | 16 |

* In the case of pigmented stock the solubility end point was the appearance of a milky color. This could not be used in the case of milled pale crepe and the end point chosen was complete dispersion.

## Effect of Alkalinity

A water suspension containing fine-particle-size zinc oxide is slightly alkaline to phenolphthalein, and in order to learn

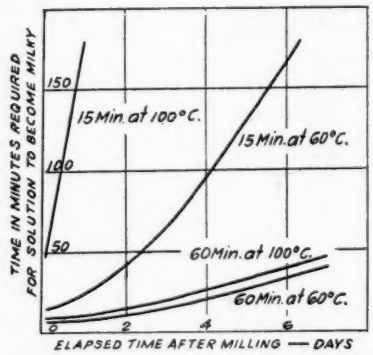



**Figure 6—Effect of Storage on Solubility of Unvulcanized Rubber**

Determinations made at room temperature 75° ± 5° F. (24° ± 3° C.)

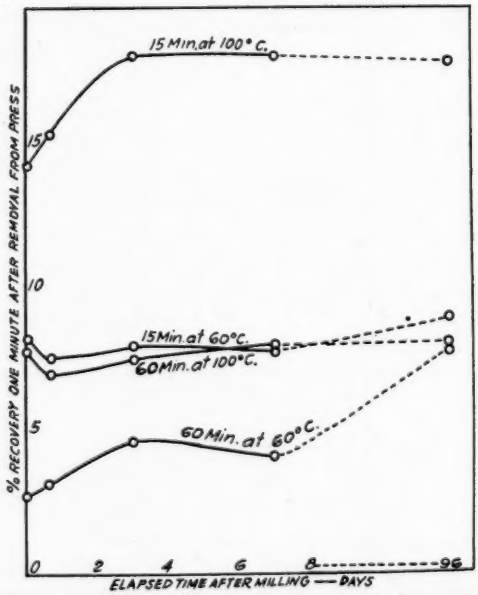



**Figure 7—Effect of Time on the Percentage Recovery after Removal from the Consistency Press**

Determinations made at room temperature, 75° ± 5° F. (24° ± 3° C.)

whether the insolubility of the stock containing it might be due to this alkalinity, a series of tests was made using whiting, ordinary zinc oxide, and blanc fixe, together with 5 per cent of lime, 5 per cent of aniline, and 0.2 per cent of sodium

hydroxide, each calculated on the rubber content of the stock. These tests showed that lime and sodium hydroxide decreased the rate of solution to only a slight degree, and that aniline had no effect.

### Tests with Pigments Other than Zinc Oxide

The conclusions in this paper have been based largely on the behavior of two zinc oxides and carbon black because there is considerable information regarding their particle size, because of the difference in the surfaces, and because their rubber stocks give a good solubility end point on account of the opacity of the pigment, but a number of tests were also made on other pigments; precipitated whiting, blanc fixe, and clay giving decreasing solubility in the above order, as would be expected with decreasing average particle size. As a test case a magnesium carbonate stock was investigated. This pigment is very badly flocculated as shown by the dryness and hardness of the stock. In spite of a particle size coarser than ordinary zinc oxide, the stock containing this sample of magnesium carbonate was decidedly insoluble as had been predicted on a basis of its poor wetting. In another test two lithopones were compared, the average particle size of one being approximately 0.3 to 0.35 micron and of the other approximately 0.4 to 0.5 micron, with aggregates considered as individual particles. These were compared for solubility in 20-volume stocks (20 volumes of pigment to 100 volumes of rubber). As was expected, the compound containing the finer lithopone required much longer (about three times) to go into solution than the one containing the coarser material. These two lithopones are approximately representative of extremes in the particle-size range of commercial lithopones.

A further consideration of the dispersion of pigments in unvulcanized rubber, for which the data are still very incomplete, would be helpful in bringing about a better understanding of the working qualities of factory stocks.

### Literature Cited

(1) Ashman and Homewood, *India Rubber World*, **77**, 59 (1928).
(2) Goodwin and Park, IND. ENG. CHEM., **20**, 621 (1928).
(3) Depew, *Rubber Age*, **24**, 378(1929).
(4) Grenquist, IND. ENG. CHEM., **20**, 1073 (1928).
(5) Meyer and Mark, *Ber.*, **61B**, 1939 (1928).
(6) Stevens, *J. Soc. Chem. Ind.*, **47**, 37T (1928).

# On the Permeability of Rubber Mixings

**W. Cecil Davey and T. Ohya**

*Introductory.*—In order to obtain the longest life for motor cover inflating airbags two features are necessary in the rubber: (*a*) that it is a mixing not readily oxidized, (*b*) that it has a low permeability. This latter point has been discussed by Daynes (*Trans. Inst. Rubber Ind.*, **3**, 438 (1928)), and it is probable that it is a very important factor as at the temperatures normally used in vulcanizing the rate of diffusion of gas through rubber is greatly increased. It is conceivable that a mix having a low permeability and poor aging would outlast one having high permeability and good aging, as in the former case the deterioration of the rubber would be kept close to the surface. As little information is available on the effect of different mixing ingredients on the rate at which a gas passes through the rubber, the experiments outlined below were made.

*Procedure.*—Different mixings were topped on to cambric by means of a factory calender. Two pieces of the canvas were then pressed face to face for use in testing. The rubber did not enter into the canvas, the latter merely acting as a support for it, and it was assumed that the canvas did not offer any resistance to the passage of a gas. Vulcanization was effected in open steam with the samples wrapped on a mandrel with lapping cloth. The permeabilities of the rubbers to hydrogen were determined by the constant flow method, using an interferometer for indication purposes.

*Principle of Testing.*—Air and hydrogen have different refractivities to light, hence the presence of hydrogen in the air will affect the refractivity. The refractivity of the mixed gas is connected with the amount of hydrogen in the air by the following formula:

$$a = \frac{760 \times T \times \Delta R \times 100}{P \times 273 \times (R_1 - R_2)},$$

where $a$ = percentage of hydrogen in the mixture; $T$ = absolute room temperature; $P$ = barometric pressure; $R_1$ = refractivity of air at 0° C. and 760 mm. ($2.926 \times 10^{-4}$); $R_2$ = refractivity of hydrogen at 0° C. and 760 mm. ($1.384 \times 10^{-4}$); and $\Delta R$ = deviation of refractivity of the mixed gas from that of air at a pressure $P$ and absolute temperature $T$. $\Delta R$ can be obtained by reference to a table showing the relation between $\Delta R$ and $\alpha$ the actual angle of rotation of the interferometer prism.

The value $a$ thus obtained is introduced into the following formula:

$$L = \frac{Q \times a}{100 \times A}$$

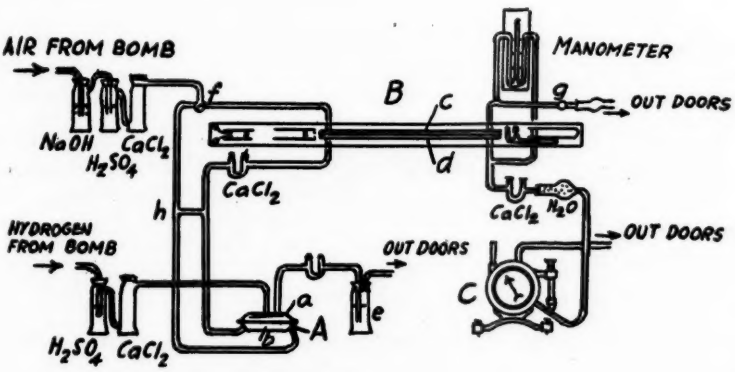
where $L$ = volume of hydrogen in liters which pass through one sq. meter of rubber membrane in a day; $Q$ = volume of the mixed gas in liters which flows through the gas meter in a day; and $A$ = area of rubber membrane in sq. meters.

*Apparatus.*—The apparatus is made up of three parts, A, B, and C. The diffusion cell (A) consists of two flat, wrought iron dishes 30 cms. internal diameter and

each having inlet and outlet pipes. The dishes are separated by the membrane under test and are capable of being made air-tight by means of bolts. The part B consists of the interferometer divided into two narrow sections (*c* and *d*), a telescope and a rotating prism, which is fitted with a device for measuring its angle of rotation. The two sections (*c* and *d*) are connected with separate manometers to adjust the pressure of gas in them, and one of the sections is connected with a gas meter (part C). The latter is fitted with a finely divided scale, the speed of the gas corresponding to one division per minute being known (33.98 liters per day).

### Testing Procedure

(1) *Adjusting the Apparatus with Air.*—The sample under test is bolted down into position and then air turned on from a bomb. The air flows through purifying and drying solutions and then separates into two streams. One flows directly to one section of the interferometer tube, thence outdoors, while the other flows through the diffusion cell to the other side of the interferometer, thence to the gas meter, and finally by a tube led outside the room. The pressure of the gases in the two sides of the interferometer should be the same and the speed of air flow practically constant during the determination. On viewing in the telescope two different spectra are seen. These are brought into exact alignment by rotating the prism, and then the scale reading $\alpha_1$ is taken.




(2) *Determination with Hydrogen.*—After the reading $a_1$ has been taken the connection is altered so that purified, dried air flows into one side of the diffusion chamber and from thence after again passing a drying tube into the interferometer, while purified dried hydrogen is admitted into the other side of the diffusion chamber from whence it escapes outside the room. During its passage some of the hydrogen diffuses through the rubber into the air on the other side, the amount of hydrogen being calculated as given above.

The pressure of hydrogen in the diffusion chamber is kept constant by regulating the head of water in a bottle through which the hydrogen escapes outside. The estimation is commenced 5 min. after constant flows of air and hydrogen are attained. Readings of the position of the prism which brings the two spectra into alignment are taken every 4 min. for 30–40 min. This reading $\alpha_2$ minus the previous reading $\alpha_1$ gives the angle ($\alpha$) of rotation brought about by the hydrogen, *i. e.*, $\alpha = \alpha_2 - \alpha_1$.

*Mixings.* (1) Rubber 100, sulfur 8.
(2) Rubber 91, zinc oxide 5, sulfur 3, ethylidene aniline 1.
(3) Rubber 100, zinc oxide 3, sulfur 3, stearic acid 2, captax 0.8.
(4) As (2) with addition of nonox $1^1/_2$.
(5) As (2) with addition of baygal $1^1/_2$.
(6) As (2) with addition of softeners 5.
(7) As (3) with addition of 10 vols. on rubber of carbon black.
(8) As (3) with addition of 10 vols. on rubber of zinc oxide.
(9) As (3) with addition of 10 vols. on rubber of Dixie clay.
(10) As (3) with addition of 10 vols. on rubber of whiting.

*Cures.*—Mix 1: (*a*) 10 min. rise, 100 min. at 50 lb.; (*b*) 10 min. rise, 200 min. at 50 lb. Mixes 2, 4, 5 and 6: (*a*) 15 min. rise, 20 min. at 40 lb.; (*b*) 15 min. rise, 4 min. at 40 lb. Mixes 3 and 7–10: (*a*) 40 min. at 20 lb.; (*b*) 75 min. at 20 lb.

*Summary of Results.*—The figures denote the number of liters of hydrogen per day which pass through one sq. meter of rubber film calculated to a thickness of 0.1 min.

| | Uncured | Cure (*a*) | Cure (*b*) |
|---|---|---|---|
| (1) | 16.95 | 35.4 | 35.2 |
| (2) | 17.5 | 28.6 | 28.7 |
| (3) | 6.35 | 10.6 | 10.8 |
| (4) | ... | 17.7 | 18.9 |
| (5) | ... | 19.5 | ... |
| (6) | 10.7 | 14.2 | 14.6 |
| (7) | 8.0 | 13.25 | 13.75 |
| (8) | (13.6) | 12.8 | 13.9 |
| (9) | 16.65 | 19.4 | 21.2 |
| (10) | 16.8 | 26.5 | 26.4 |

*Conclusions.*—The results with the uncured rubber are irregular probably due to variability in thickness of the soft rubber near the bolts of the diffusion chamber. It is clear that vulcanizing increases the amount of gas which passes through the rubber, but there is little difference between the figures for the two cures. The cured accelerated mixings give much lower figures than the plain rubber-sulfur mixing. Softeners (and antioxidants) cause still lower figures (it is probable that much of the low figure for the captax mixing is due to the stearic acid). The effect of adding mineral fillers is in all cases to assist the passage of gases, although the fine fillers, zinc oxide and carbon black, do not have much effect in this respect.

The authors' thanks are due to the Imperial Industrial Laboratory, Osaka, for use of the laboratories in which the tests for this investigation were made.

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[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 12, page 1215. December, 1929.]

# Permeability of Rubber to Air

## I—Effect of Temperature, Pressure, and Humidity[1]

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**Apparatus and procedure are described for investigating the influence of temperature, pressure, and humidity upon the capacity of rubber membranes to retain air under pressure.**

**The relation between total pressure and permeability has been found to be almost linear, the permeability being approximately proportional to pressure. The temperature coefficient of permeability is very high, thus indicating that the pressures of inner tubes should be checked much more frequently in summer than in winter. Moisture has been found to decrease the permeability of rubber to air slightly under certain circumstances. Prolonged immersion of the rubber in water, however, resulted in an appreciable increase in permeability.**

ALTHOUGH it has been nearly a century since Mitchell (*14*) and Cagniard-Latour (*2*) reported their experiments on the passage of gases through rubber, it was not until relatively recent years that any practical interest in the phenomenon was aroused. This interest was first occasioned by observations on the tendency for hydrogen to diffuse through the rubber membranes of balloons. At present the permeability of rubber to gases is of much more general interest, since it is a factor of prime importance in connection with many of our modern products, such as automobile inner tubes, dirigibles, gas masks, tennis balls, other balls for athletic contests, etc.

[1] Presented before the meeting of the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, N. J., September 26 to 28, 1929.

As a preliminary step to a more comprehensive study of the permeability of rubber stocks to air, it was considered desirable to establish the effect of experimental conditions, such as temperature, pressure, and humidity of the atmosphere, upon permeability.

## Previous Work

Previous investigations in this field have not been extensive. Much of the work that has been done has been carried out in connection with the hydrogen-retaining capacity of balloon fabrics, and therefore does not contribute any conclusive evidence regarding the air-retaining capacity of rubber membranes. As has been recently mentioned by Daynes (*4*) in his excellent review of the permeability of rubber to gases, the textiles in balloon fabrics exert such a marked influence on permeability that conclusions from work on balloon fabrics cannot safely be extended to rubber films.

In regard to the effect of temperature, Graham (*9*) observed in 1866 that the permeabilities of a given rubber specimen at 4°, 14°, and 60° were in the ratio of 1 : 4 : 11.8. In more modern times Daynes (*3*) and Edwards and Pickering (*8*) have also observed a marked temperature coefficient for permeability. Kayser (*12*) has reported results for the diffusion of hydrogen and carbon dioxide, which, when extrapolated, are capable of leading to the conclusion that the permeability of rubber to these two gases is zero at 0° C. Dewar (*5*), however, has observed a definite diffusion of gases through rubber at temperatures well below 0° C.

In his curves coördinating temperatures and logarithms of rate of diffusion through rubber, Dewar (*5*) found such a break at 0° C. that he was naturally led to associate the moisture content of the rubber with its permeability. When he continued his experiments to include water vapor itself, he found this substance to diffuse through rubber at a very rapid rate. This observation has been verified by Edwards and Pickering (*8*), Schumacher and Ferguson (*15*), and others. Certain interesting observations made by Lowry and Kohman (*13*) on the mechanism of the absorption of water by rubber are mentioned later in this report. In regard to the possible effect of the humidity of the atmosphere on the permeability of rubber to air, Dubosc (*6*) quoted Victor Henry to the effect that humidity influences the permeability of balloon fabrics. Edwards (*7*), on the other hand, found humidity to be of very little influence.

The observations of Edwards and Pickering (*8*) on the effect of pressure up to 100 mm. of water are of little significance in connection with the present study. Wroblewski (*16*) stated that the diffusion of carbon dioxide or hydrogen through rubber was proportional to the pressure of the gas. This observation was later verified by Kayser (*12*). Dewar (*5*) found, however, that as pressures were increased from

1 to 20 atmospheres the rate of diffusion of these two gases increased at a more rapid rate than did the pressure.

It is not intended in this first report to go very profoundly into the theory of permeability of rubber to gases. It may be mentioned that Graham (*9*) considered the phenomenon to be one involving solution of the gas in the rubber, diffusion of the dissolved or liquefied gas, and evaporation on the opposite side. Later investigators have, in general, accepted Graham's hypothesis. That an actual porosity of a type may also be a contributing factor in the case of certain rubber stocks seems probable to the authors.

## Experimental Method and Apparatus

The apparatus used in this study represents an alteration of an earlier one developed by R. W. Brown, of the Experimental Engineering Department of this company. The method of measurement was essentially a manometric one. Air, under pressure, in one chamber was allowed to permeate into another chamber through the rubber slab being tested. A manometer sealed to the slab allowed the change in pressure to be followed.

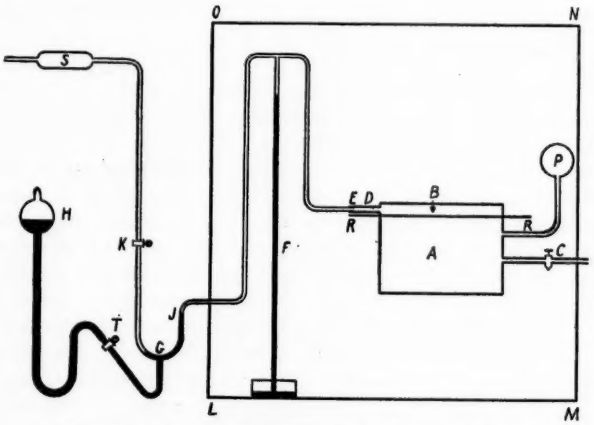


**Figure 1—Apparatus for Measuring Permeability**

The essential features of the apparatus, which has been designated as a permeameter, are shown in Figures 1 and 2 (glass part not completely shown in Figure 2). The two air chambers, set in rather heavy iron castings, are indicated by *A* and *B*. A screw clamping arrangement permitted the two chambers to be drawn together as tightly as desired on the rubber slab, *RR'*. The latter was also held in position at its ends by clamps (Figure 2), whose distance apart was adjustable. It was thus possible to stretch the rubber in one direction to the extent of about 40 per cent. A pressure gage, registering from 0 to 100 pounds per square inch (0 to 7.03 kg. per sq. cm.), is designated by *P*. The brass tube, *D*, from

the chamber *B* was sealed with wax at *E* to the glass manometer system, *F*. As the changes in pressure during any experiment were very small, it was possible to use mineral oil as a manometer fluid. In order to avoid any difficulty from leaking stopcocks, the system was closed by the mercury seal at *G* prior to the beginning of any determination. The drying tube, *S*, contained soda lime. A wooden case, within which it was possible to maintain a fairly constant temperature by means of heating units, a fan, and a suitable thermostatic device, is indicated by LMNO. For runs of short duration, such as those reported below, hand operation of the heating device was found to give satisfactory control of temperature. The front of the case was provided with glass windows, arm holes, and rubber sleeves, so that it was possible to manipulate the apparatus without disturbing the temperature control.

The rubber membranes used in most of this study were prepared from a pure-gum mixture containing 2.89 per cent of both sulfur and zinc oxide, and 0.63 per cent of di-*o*-tolylguanidine. They were cured in specially made molds in a press at 149° C. for 30 minutes, unless otherwise specified. The test slabs had an average thickness of 0.07 cm.

In making a measurement the rubber slab, which had usually been dried over soda lime for several days, was placed in the clamps. The rubber was ordinarily stretched as much as it was possible to stretch it by adjusting the position of the clamps. The effect of stretch was counterbalanced somewhat by the contraction which tended to occur at right angles to the direction of stretch. The two chambers were then drawn together over the rubber slab. A gasket of rubber was used around the base of the upper chamber to prevent injury to the slab being tested. Compressed air, dried as completely as possible by passage through a metal tube filled with soda lime, was introduced slowly through the valve, *C*. A rather arbitrarily selected gage pressure of 46 pounds per square inch (3.23 kg. per sq. cm.) was used in chamber *A* during most of the experiments. A fairly heavy metal gauze across the base of the low-pressure chamber, *B*, served as a support and thus prevented too great a distension and possible rupture of the rubber slab. This gauze, by being in contact with the rubber membrane, undoubtedly exerted some influence on the absolute value of permeability obtained. With *K* and *G* both open, a slight suction was applied through *S* and the manometer fluid lifted to a definite height. *K* was then closed and *H* lifted until the mercury rose to a definite point, *J*. Before reading the manometer at any time thereafter, the mercury level was always brought exactly to the point *J*. The usual procedure consisted in making readings of the manometer every 3 minutes. When the rate of fall in the manometer became constant, the average for several successive readings was taken as the value to be used in calculating permeability. Strictly speaking, the

rate of fall should never become constant, as the pressure difference on the two sides of the rubber slab is constantly decreasing, and the composition of the air on the high-pressure side is constantly changing as a consequence of the greater permeability of rubber towards oxygen than towards nitrogen. The influence of these factors is negligible, however, during the course of any single measurement.

The factors which tend to militate against a high accuracy in these experiments are rather numerous. Even in the case of a test specimen which is tested several times while standing undisturbed in the permeameter, small variations in the temperature, pressure, time subsequent to stretching, and degree of stretch (slippage) may influence the values. If the slab is removed from the permeameter between tests, possible variation in the exact portion being tested is of considerable importance. In the case of a blooming slab, interference by the bloom with a proper seal at the gaskets is a possible source of error. In the case of slabs tested from day to day, variations in aging, humidity, etc., are added to the above-mentioned factors. Several additional possibilities are encountered in the cases of slabs cured at different times or from different mixes. In general, however, it has been possible to check results within 5 per cent. Although it is possible under the best conditions to obtain values which are reproducible within 1 or 2 per cent, it is improbable that the absolute accuracy of the measurements is ever much under 5 per cent.

Two calculations were made throughout the experiments. One was that necessary to convert the actual reading taken into units of volume per unit of time per unit of surface exposed. Calibrations of the apparatus indicated that the factor 0.90 will convert centimeters per minute on the manometer to liters of air per hour per square meter of rubber exposed, the volume being that existing under a pressure equivalent to that of the atmosphere. The volume obtained in the above calculation was then corrected to standard barometric pressure. All values shown in the experimental part have already been corrected to a barometric pressure of 760 mm.

### Effect of Pressure on Permeability

For the purpose of studying the effect of pressure on permeability, a rubber slab was put in the apparatus, stretched, and left stretched overnight previous to starting the experiments. The measurements reported in Table I were all made on the same day without moving the slab from the permeameter. Since the slab had been cured 25 days before use, any change in permeability due to aging during the course of the experiments was undoubtedly negligible. The average thickness of the slab used, when measured unstretched, was 0.066 cm. (0.026 inch). A temperature of 35° C. (95° F.) was maintained. The pressure difference as given in Table I represents the gage pressure plus the slight vacuum on the low-pressure side. Pressures given in all subsequent work refer

to gage pressures only. The results are shown in Table I and graphically in Figure 3.

It is apparent from Figure 3 that the relation between pressure and permeability is almost linear. The rate of increase of permeability with pressure becomes slightly greater, however, as the pressure increases. Another series of measurements made on a different slab gave a similar curve, but one showing a slightly greater change in rate as the pressure increases. The results thus obtained tend to confirm those of Dewar (*5*) rather than those of other investigators who concluded that permeability is an exactly linear function of pressure. In connection with the present experiment (and those of Dewar as well) it seems possible that the deviation from a straight line may be due to an increased distension of the rubber at the higher pressures. Although the membrane was protected by a metal gauze, it could have been pressed into the interstices in the gauze sufficiently to reduce its thickness and consequently increase its permeability slightly.

**Table I—Effect of Pressure on Permeability**

| Pressure Difference | | Permeability |
|---|---|---|
| *Lbs. per sq. in.* | *Kg. per sq. cm.* | *Liters per hour per sq. m. surface* |
| 59.3 | 4.17 | 0.35 |
| 47.3 | 3.33 | 0.28 |
| 36.5 | 2.57 | 0.20 |
| 24.6 | 1.73 | 0.13 |
| 10 5 | 0.738 | 0.05 |
| 23.6 | 1.66 | 0.14 |
| 36.3 | 2.55 | 0.19 |
| 44.4 | 3.12 | 0.25 |

## Effect of Temperature on Permeability

The same rubber slab was used as in the work previously reported. The procedure was also the same except that the pressure was maintained constant at 46 pounds (3.23 kg. per sq. cm.) on the gage while the temperature was varied. The pressure was released, however, and a new supply of air taken in before each determination. More time was required for each run during this investigation, as the heavy metal apparatus attained the desired temperatures but slowly. Several of the results tabulated below represent the average of two or more determinations. The results are shown in Table II and graphically in Figure 4.

**Table II—Effect of Temperature on Permeability**

| Temperature | | Permeability |
|---|---|---|
| *° C.* | *° F.* | *Liters per hour per sq. m. surface* |
| 25.7 | 78.2 | 0.16 |
| 27.0 | 80.6 | 0.18 |
| 28.0 | 82.4 | 0.19 |
| 29.0 | 84.2 | 0.20 |
| 31.0 | 87.8 | 0.23 |
| 34.0 | 93.2 | 0.27 |
| 37.0 | 98.6 | 0.31 |
| 40.0 | 104.0 | 0.37 |

Measurements were made at higher and lower temperatures than those recorded. The values obtained were not

acceptable, however, as the temperature control was not satisfactory. The curve obtained shows a qualitative similarity to those of Kayser (*12*) and Edwards and Pickering (*8*) for carbon dioxide and hydrogen. The curves of these investigators, who covered a wide temperature range with very few experimentally determined points, resemble throughout what was anticipated for the present curve—i. e., that the rate of change of permeability with temperature decreases as the temperature is lowered from 25° C. to 0° C., while it remains practically the same above 40° C. as it is at that temperature. It is regretted that facilities were not available for satisfactorily studying the effect of temperature over a wider range.

The above results indicate that a wide variation exists between the permeabilities of the same inner tube in winter and in summer. For the purpose of a more definite comparison a climate may be considered whose maximum temperature variation during a year is from 5° F. to 95° F., a range greatly exceeded in certain parts of the United States. As may be seen from Figure 4, the permeability is reduced by about 50 per cent in lowering the temperature from 95° F. to 75° F. In this connection it may be mentioned that Kayser (*12*) found the permeability towards carbon dioxide to decrease by 77 per cent when the temperature was lowered from 91° F. to 48° F., and Graham (*9*) obtained a twelvefold increase by raising the temperature from 39° F. to 140° F. It is obvious that permeability will be very low when the temperature is lowered to 5° F., or even to 32° F. The above considerations hold for a tube that is not otherwise heated than by atmospheric conditions. Certain experiments performed by our laboratories indicate that heavy-duty inner tubes may attain a temperature somewhat above the boiling point of water under extreme conditions on a hot summer day. The maximum temperature to which passenger tubes are subjected is somewhat lower. The permeability at such high temperatures is undoubtedly many times the highest permeability measured in the present experiments. Edwards and Pickering (*8*), for instance, found the permeability of rubber to carbon dioxide to be 3.5 times as great at 212° F. as at 95° F. The higher pressures accompanying higher temperatures further increase the rate of deflation. The conclusion is inevitable that pressures must be watched much more closely in summer than in winter if the evil consequences of underinflation are to be avoided.

### Effect of Moisture on Permeability of Rubber to Air

In view of the difficulty, as reported by Edwards and Pickering (*8*), of obtaining any accurate determination of the permeability of rubber to water vapor itself, the evaluation of the effect of moisture on the permeability to air was not expected to be an easy task. In the present experiments comparisons were made between the permeabilities of rubber

slabs in a desiccated condition and after having been (*a*) painted with water, (*b*) soaked in water, or (*c*) exposed to atmospheres of various relative humidities. As a final step, a study was made of the effect of compounding agents whose function was to render the rubber more hygroscopic and therefore more capable of being influenced by moisture.

In a preliminary test the permeability of a given slab was measured after it had been exposed to air for several days, and again immediately after it had been painted with water on the high-pressure side. The permeability to air was 8 per cent less in the second case. In a repetition of this comparison, made 6 months later, very little difference was noted between the value for the permeability before and after coat-

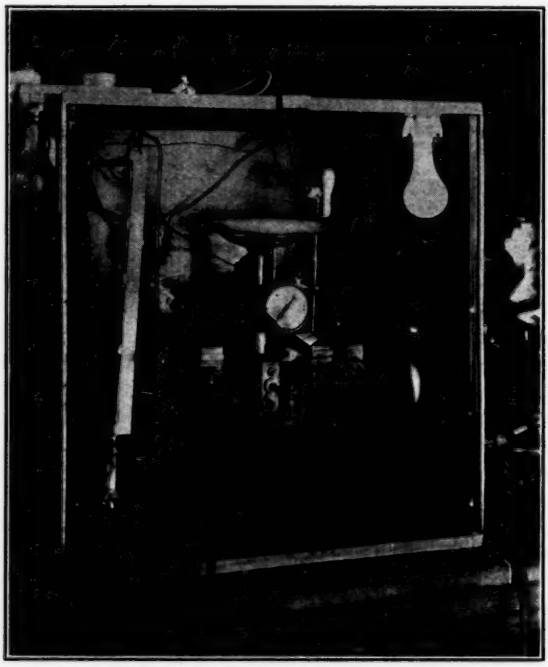

**Figure 2—Assembled Apparatus for Measuring Permeability**

ing the slab with water. Since the permeability in each case was determined immediately after painting the slab with water, the latter could have had no material effect on the rubber itself. Whatever effect the water may have had in decreasing permeability was probably due to its ability to decrease the concentration of gaseous molecules in contact with the rubber.

After the above-mentioned results had been obtained, it was reasoned that a greater difference should exist between

dry and wet slabs, provided the former were actually dried out in a desiccator prior to being tested. In this connection, attention should be called to the observations of Lowry and Kohman (*13*) that absorption of water is at the same rate when rubber is immersed as when suspended in vapor at the same pressure as the vapor pressure of the immersing medium. It is thus obvious that a rubber slab would be in practically the same condition after being exposed to an atmosphere of very high relative humidity as it would be after being immersed in liquid water for the same period of time. In continuing the study, therefore, a rubber slab cured for 80 minutes at 143° C. was stored over soda lime for several days. Its permeability in the unstretched condition was then measured at 30° C. and 46 pounds per square inch (3.23 kg. per sq. cm.) pressure. Subsequent determinations on permeability were made after the slab had been given the following successive treatments: immersed in water overnight, ex-

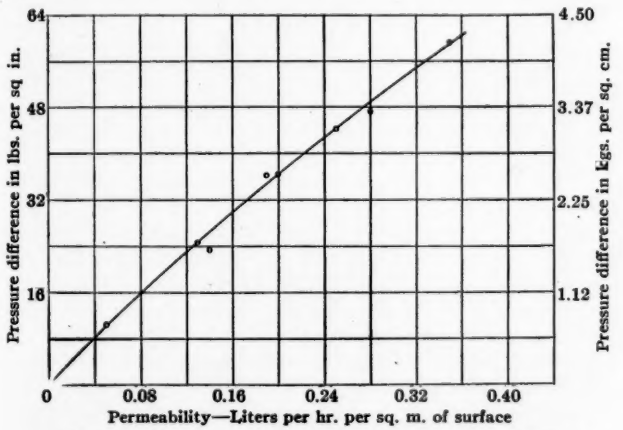


**Figure 3—Relation between Pressure and Permeability**

posed to the air 24 hours when the relative humidity was about 20 per cent, stored over soda lime 14 days, and immersed in water for 15 months. Before testing the sample after immersion, the free water was removed from the surfaces as thoroughly as possible by the use of paper towels. The results of the various measurements are shown in Table III.

**Table III—Effect of Moisture on Permeability of Rubber to Air**

| Permeability | Treatment Prior to Test |
|---|---|
| *Liters per hour per sq. m. surface* | |
| 0.15 | Over soda lime 1 week |
| 0.11 | Immersed in water 16 hours |
| 0.13 | Exposed to air 24 hours (rel. hum. 20%) |
| 0.13 | Over soda lime 2 weeks |
| 0.18 | Immersed in water 15 months |
| 0.16 | Dried to constant weight |

The results indicate that a short period of immersion in water reduces the permeability, but that prolonged immersion

increases it appreciably. The accuracy of the last value obtained is more open to question than that of the others, since the apparatus had been modified slightly in the interim and the rubber sample had undergone some change. Natural aging during the period of 15 months must have exerted some influence on the permeability. Edwards and Pickering (*8*) found, however, that the permeability was decreased rather than increased by natural aging up to the point where the rubber began to crack.

The dimensions of the test sample were increased by the long immersion, the average thickness changing from 0.071 cm. to 0.082 cm., and the length and width increasing by 2 or 3 per cent. This loosening of the structure of the rubber as a consequence of immersion is probably the major factor in the increased permeability. The reappearance under the microscope of the individual latex particles in crude rubber as a consequence of boiling with water has been described by Grenquist (*10*) and discussed by Hauser (*11*). The swelling of the proteins and resins probably changes their indices of refraction sufficiently to account for the result obtained under the microscope. The expansion of the vulcanized sample used in the present study indicates that a similar change, to some degree at least, had taken place in it during immersion in water for 15 months. If such is the case, the opportunity for the gaseous molecules to diffuse around the rubber particles by passing through the swollen non-rubber constituents is much greater than is the case with a dry sample. The decrease in the rigidity of the sample as a whole as a consequence of immersion is, moreover, another factor of considerable importance in connection with the resistance offered to the passage of gaseous molecules.

When the sample was dried to constant weight for the last test its loss in weight was 9.0 per cent. The observed decrease in permeability on drying again to constant weight was in accordance with expectations.

In a final comparison of this general nature, a slab was tested after it had been stored over soda lime for several months. The air used in this test was passed very slowly through the drying tube into the permeameter. The value for the permeability of the unstretched slab at 30° C. and 46 pounds (3.23 kg. per sq. cm.) was 0.15. Immediately after this test, a small vessel containing water was inserted into the high-pressure chamber of the permeameter, the slab was clamped into position, and the system allowed to stand under 46 pounds pressure for 18 hours. The permeability then, when corrected for the slight loss in pressure, was 0.13. The formation of rust on the walls of the permeameter may have been sufficient to change the composition of the gaseous mixture enough to account for most of the reduction noted. In this connection it should be mentioned that other investigators have found oxygen to diffuse nearly three times as rapidly through rubber as does nitrogen.

It seemed reasonable to expect that, the greater the hygroscopicity of a stock, the greater should be its susceptibility to the influence of atmospheric moisture. The addition of 5 per cent of finely ground anhydrous calcium chloride to the previously described rubber compound was the only method of increasing hygroscopicity used which yielded a set of results worthy of record. The success attained by Lowry and Kohman (*13*) in altering the water absorption of a thoroughly washed rubber by milling sodium chloride into it is worthy of mention in this connection. The presence of the calcium chloride in the experimental stock of the present test so increased the time of cure that the slab cured for 60 minutes at

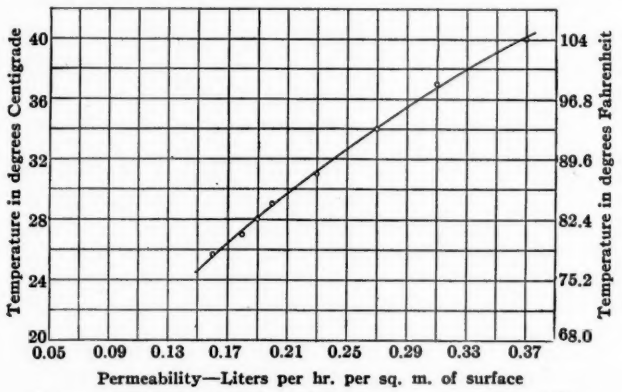


**Figure 4—Relation between Temperature and Permeability**

160° C., and used in the test, was apparently undercured. This slab was placed in a desiccator over calcium chloride immediately after being cured. The results of permeability tests carried out in the usual manner are shown in Table IV.

**Table IV—Effect of Humidity of Air on Permeability of a Rubber Stock Containing Calcium Chloride**

| PERMEABILITY *Liters per hour per sq. m. exposed* | TREATMENT PRIOR TO TEST |
|---|---|
| 0.19 | Stored over $CaCl_2$ |
| 0.18 | Exposed to atmosphere 2 hours, (rel. hum. 26%) |
| 0.19 | Exposed to atmosphere 20 hours |
| 0.16 | Exposed to satd. atmosphere 4 days |
| 0.17 | Exposed to satd. atmosphere 8 days |

In drawing conclusions from these various comparisons it seems to be justifiable to state that moisture is capable of affecting the permeability of rubber to air. The effect of the moisture in the atmosphere is small, however.

**Acknowledgment**

The authors wish to acknowledge their indebtedness to N. A. Shepard for counsel and to the Experimental Engineering Laboratory of this company for assistance in the construction and maintenance of the apparatus.

## Literature Cited

(1) Anon, *India Rubber J.*, **76**, 217 (1928).
(2) Cagniard-Latour, *J. Franklin Inst.*, **24**, 117 (1839).
(3) Daynes, *Proc. Roy. Soc.* (*London*), **97A**, 286 (1920).
(4) Daynes, *Trans. Inst. Rubber Ind.*, **3**, 428 (1928).
(5) Dewar, *Proc. Roy. Inst. Gt. Brit.*, **21**, 813 (1915).
(6) Dubosc, *Rev. gén. caoutchouc*, **39**, 7 (1928).
(7) Edwards, *India Rubber J.*, **56**, 821 (1918).
(8) Edwards and Pickering, Bur Standards, *Tech. Bull.* **387** (1920).
(9) Graham, *Trans. Roy. Soc. London*, **156**, 399 (1866).
(10) Grenquist, IND. ENG. CHEM., **21**, 665 (1929).
(11) Hauser, *Kautschuk*, **5**, 151 (1929).
(12) Kayser, *Ann. Physik*, **43**, 544 (1891).
(13) Lowry and Kohman, *J. Phys. Chem.*, **31**, 23 (1927).
(14) Mitchell, *Am. J. Med. Sci.*, **7**, 36 (1830).
(15) Schumacher and Ferguson, IND. ENG. CHEM., **21**, 158 (1929).
(16) Wroblewski, *Pogg. Ann.*, **158**, 539 (1876).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 10, page 911. October, 1929.]

# Some Observations on Carbon Black[1]

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**Different carbon blacks have certain definite effects upon the vulcanized rubber stocks with which they are mixed. The experiments described herein may be grouped under four main heads: (1) adsorption, (2) effect of heat, (3) reaction with sulfur and zinc oxide, and (4) dispersion or rate of settling.**

**The adsorptive capacity of the black is a measure of the rate of cure of the rubber mix, low-adsorptive blacks giving a faster curing stock than high-adsorptive blacks. An indication of the stiffening action of a carbon black may be secured by measuring the amount of carbon dispersed in a thin rubber cement which cannot be centrifuged out in a given time. The effect of temperatures from 500° to 1200° C. on carbon blacks is to render them highly adsorptive and also to give a rubber mix which cures faster and has a higher modulus. The reaction of carbon blacks with sulfur and zinc oxide in boiling xylene liberates a substance having accelerating properties in a pure gum mix.**

THE peculiarities of this interesting, unpleasant, but wholly necessary material have been thoroughly studied by its producers and consumers. Its related substances, charcoal and lampblack, have been the subject of theoretical research for many years. In the course of some work recently carried out in the writers' laboratories some interesting observations have been made. These have not been studied exhaustively, nor can definite conclusions applicable to all types and classes of blacks be drawn, but the results seemed to be of sufficient importance to record in this paper.

[1] Presented before the Division of Rubber Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

## Historical

It has been noticed for several years, in compounding carbon blacks, that different rates of cure of the rubber stock are obtained with different blacks. The general opinion is that these differences are caused by adsorption of sulfur and accelerator by the blacks, and that a determination of the adsorption value would show the approximate action of a black on the cure of a rubber mix.

Leblanc, Kroeger, and Kloz (*6*) concluded that it was not possible to predict the properties of a rubber-black mix from a study of the crude black. Spear and Moore (*7*) decided that adsorptive capacity and other tests on the black were not sure indications of the quality of a stock. Recently Goodwin and Park (*4*) have stated that "adsorption is the one property of carbon blacks that exerts the profoundest influence upon the character of a rubber mix," while Beaver and Keller (*2*) state that "no correlation could be found between iodine adsorption and the effect of these blacks on the rate of cure." The results of the present work are in agreement with the opinion of Goodwin and Park.

In regard to the effect of heat on blacks, Johnson (*5*) has found that blacks having a low percentage of volatile material at 900–1000° C. are of higher quality in a rubber mix than those having high volatile matter. Likewise, Beaver and Keller have found that blacks of low oxygen content give a fast curing stock.

The writers are not aware of any published work backed by experimental data on the relation of dispersion of carbon blacks to any properties of the rubber with which it is mixed. However, an article of Stamberger (*8*) on the rate of settling and dispersion of various pigments (including carbon black) in dilute rubber cements led to an investigation along similar lines. It is the purpose of this paper to show, among other things, that there is a remarkable relationship between degree of dispersion and modulus, but that rate of settling is seldom indicative of differences in physical properties of the cured stock.

## Experimental Procedure

In the study of adsorption by carbon blacks the method of Bartell and Miller (*1*) using benzoic acid was first followed; later the use of iodine solutions, as suggested by Davis (*3*), was adopted. In the course of the work a number of variables were found which might affect the results. The effects of time, temperature, concentration of solutions, weight of sample, presence of inorganic salts, and pH of water used in making up standard solutions have all been taken into account. However, for purposes of comparing commercial blacks it was found possible simply to establish a standard procedure and follow it in all cases.

BENZOIC ACID METHOD—0.25 gram of the black was weighed into a bottle, 50 cc. of standard benzoic acid solution added,

and adsorption allowed to take place with shaking from 10 to 30 minutes. The solution was filtered quickly into a buret, 25 cc. run out into a beaker and titrated with sodium hydroxide solution of approximately the same normality, using phenolphthalein as an indicator. To correct for benzoic acid adsorbed by the filter paper, the blank was also filtered, and the difference between the titration figure of blank and sample was a measure of the acid adsorbed by the black. The result was expressed in grams of benzoic acid per gram of black. The titrations were made at three or more different concentrations and the adsorption curves of four different blacks are plotted in Figure 1.

IODINE METHOD—Iodine was found to be somewhat more easily adsorbed than benzoic acid, giving a larger scale to work over. Hence the rest of the experiments were made with iodine. Iodine solutions were made up in several concentrations using a little potassium iodide to aid solution, 0.25 gram of black was weighed into an oil sample bottle, 50 cc. of standard iodine solution added, and the bottle shaken for 10 to 20 minutes. It was then centrifuged for 5 minutes to throw all the black to the bottom. 25 cc. were then pipetted out and titrated with sodium thiosulfate solution of about the same normality as the iodine. The initial concentration of the iodine was determined by a blank, the difference being the iodine adsorbed by the black. The result was calculated to grams of iodine per gram of black. The adsorption of iodine by several blacks plotted against end concentration is shown in Figure 2. The logarithmic diagram of a true adsorption curve is a straight line, according to Freundlich. Figure 3 shows the logarithmic curves of the blacks plotted in Figure 2.

BLACKS STUDIED—A variety of blacks was secured—two channel blacks, two grades of Thermatomic, one varnish black, and three high-temperature blacks.

These blacks were compounded in the following standard test formula: rubber 100; black 36; zinc oxide 5; stearic acid 4; sulfur 3.5; Captax 1.2. The standard black was taken as Micronex, which gave a best cure in 60 minutes at 125° C. in the above stock. In Table I an average iodine adsorption figure is taken for each black and compared with the time of best cure of each stock. The figures for modulus and tensile are also added.

**Table I—Properties of Blacks Studied**

| BLACK | IODINE ADSORBED PER GRAM BLACK | BEST TECHNICAL CURE AT 125° C. | MODULUS AT 500% | TENSILE |
|---|---|---|---|---|
| | *Gram* | *Minutes* | *Kg./sq. cm.* | *Kg./sq. cm.* |
| Thermatomic regular | 0.05 | 30 | 110 | 275 |
| Thermatomic special | 0.06 | 30 | 110 | 255 |
| Goodwin | 0.07 | 30 | 207 | 290 |
| Acetylene | 0.09 | 40 | 200 | 255 |
| Micronex | 0.09 | 60 | 194 | 305 |
| Cabot | 0.10 | 50 | 195 | 320 |
| Super-Spectra | 0.20 | 105 | 165 | 295 |
| Experimental black | 0.13 | 40 | 186 | 310 |

## Adsorption

The relationship between adsorption and rate of cure is obvious, while the lack of regularity between either modulus or tensile and adsorption needs no further discussion. The experimental black failed to line up with the others, possibly because it was simply a laboratory sample and not a perfected factory product. Blacks from the same source showed no difference in rate of cure so that no figures comparing adsorption and cure are presented.

The varying adsorption of accelerator by different blacks is shown by the following experiment: A solution of mercaptobenzothiazole in 1 part of alcohol and 2 parts of water of about 0.01 normality was prepared. The amount of accelerator was determined by titration with 0.01 *N* sodium hydroxide using phenolphthalein indicator. A similar solution of diphenylguanidine was made up and its concentration determined by titration with alcoholic hydrochloric acid using

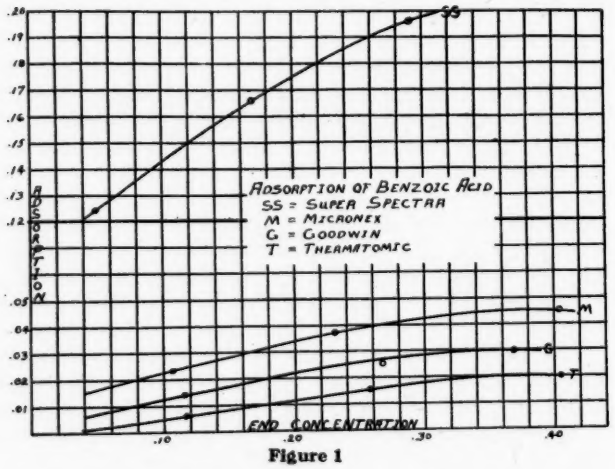


**Figure 1**

bromophenol blue indicator. The adsorption of four blacks was then determined, with the results shown in Table II.

**Table II—Adsorption of Accelerator by Different Blacks**

| Black | Adsorption per Gram of Black | |
|---|---|---|
| | Mercapto | D. P. G. |
| | *Gram* | *Gram* |
| Super-Spectra | 0.131 | 0.101 |
| Micronex | 0.030 | 0.039 |
| Goodwin | 0.009 | 0.008 |
| Thermatomic | 0.004 | 0.008 |

These figures indicate that differences in rate of cure are at least partly due to adsorption of accelerator.

## Effect of Heat

It has been stated previously that the work of Johnson in differentiating between high- and low-quality blacks by their

percentage of volatile combustible matter led to the opinion that heat treatment might give better quality.

ACTIVATION BY STEAM—The original idea had been to activate black by superheated steam, thus removing air and adsorbed hydrocarbons. An apparatus was set up consisting of an iron pipe heated by an electric combustion furnace set vertically. Steam was superheated in a copper coil and passed in at the bottom of the pipe. A thermocouple was inserted in the upper half of the black and temperatures of 550–750° C. were obtained. Micronex, when so treated for 3 hours, was found to have twice the adsorptive capacity for iodine that unactivated Micronex had. The rate of cure was somewhat faster and the modulus slightly higher than the control. Thermatomic blacks could not be activated at these temperatures. As about ten runs of the small activating unit were required to supply enough black for compounding purposes, this experiment was abandoned for one in which a large sample could be prepared in one run.

HEATING UNDER REDUCED PRESSURE—The object of this experiment was to remove adsorbed gases or moisture and to protect the black from re-adsorption of other substances during subsequent milling and curing operations. Two hundred and fifty grams of Micronex were evacuated at 10 mm. for 3 hours at 200–220° C. After cooling, and without releasing the vacuum, a solution of 75 grams of mineral rubber in xylene was added. After thoroughly mixing, the xylene was distilled off under reduced pressure. When compounded in a rubber stock, this black was not different from the untreated control, containing mineral rubber mixed on the mill.

EFFECT OF HIGH TEMPERATURE—The amount of volatile combustible matter in different blacks varies according to the temperature at which the black was made, as would be expected. Table III shows results on several blacks, the determination being made by the standard A.S.T.M. method for coal.

**Table III—Effect of High Temperature on Volatile Matter**

| BLACK | VOLATILE MATTER *Per cent* |
|---|---|
| Acetylene | 0.40 |
| Thermatomic regular | 0.75 |
| Thermatomic special | 1.30 |
| Goodwin | 1.82 |
| Experimental black | 2.16 |
| Super Spectra | 5.17 |
| Cabot, high-quality | 4.33 |
| Cabot, low-quality | 7.08 |
| Micronex, high-quality | 4.40 |
| Micronex, low-quality | 6.82 |

Without considering any other causes of variation, it seems that blacks made at higher temperatures (1000–1200° C.) are ordinarily better stiffening agents than channel blacks. A comparison of the complete stress-strain curve shows this distinctly. That the high-temperature Thermatomic blacks do not give increased stiffening to a rubber mix must be due to increased particle size.

The possibility and means of improving low-quality carbon blacks by heat treatment should be considered. For channel blacks, the writers agree with Johnson that the test is a measure of the quality of blacks for use in rubber. But for other types of black the difference would probably be too small to serve as an indication of quality.

Micronex was heated in large covered alundum crucibles in an electric furnace at 900–1000° C. for various periods from 10 to 60 minutes. Heating was found to increase the iodine adsorption in all cases, evidently by the removal of adsorbed material. However, instead of giving a slower curing stock, due to adsorption of sulfur and accelerator, it was found that the rate of cure was markedly increased and in some cases a slightly stiffer stock was obtained. The black itself, after heating, had a dry, cindery appearance and feel in contrast to the velvety feel of ordinary black. It settled very rapidly in organic liquids and seemed to be badly agglomerated. When milled into rubber it was very difficult to disperse.

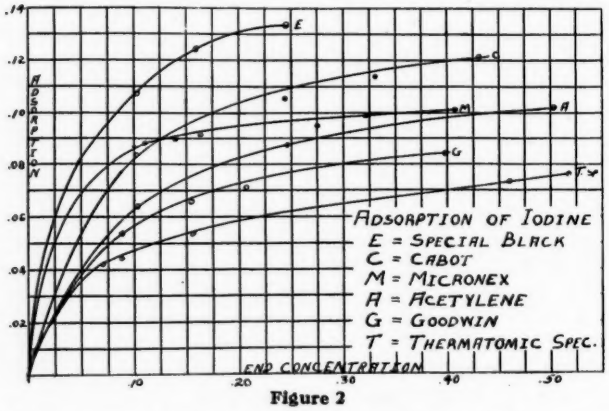


**Figure 2**

Table IV presents the data in regard to this experiment. The stock is the standard test stock, with Captax acceleration.

**Table IV—Effect of Heat Treatment on Low-Quality Blacks**

| Stock | Best Technical Cure at 125° C. | Modulus at 500% | Tensile | Elongation | Iodine Adsorption |
|---|---|---|---|---|---|
| | *Minutes* | *Kg./sq. cm.* | *Kg./sq. cm.* | *Per cent* | *Gram* |
| Control | 75 | 188 | 324 | 690 | 0.09 |
| Heated 60 minutes at 950° C. | 60 | 195 | 312 | 665 | 0.13 |
| Heated 10 minutes at 950° C. | 45 | 197 | 327 | 660 | 0.16 |
| Check on above one week later | 45 | 191 | 316 | 675 | 0.15 |

It will be seen that there is a decided increase in rate of cure and a corresponding increase of adsorptive capacity of the black with some difference in modulus or tensile of the stock as shown in Figure 4. This is, of course, a glaring exception to the previous statement, that high adsorption means slow cure. The writers have no explanation for this behavior.

## Reactions with Sulfur and Zinc Oxide

The reaction products of accelerators with sulfur and zinc oxide have often been isolated by boiling in xylene at 138° C., which is about the temperature of the 40-pound (2.1 kg. per sq. cm.) cure. Twenty-five grams of black, 10 grams zinc oxide, and 5 grams sulfur were boiled in 300 cc. of xylene for 4 hours. The xylene was then decanted, fresh solvent added, and the process repeated several times. Some of the blacks gave very highly colored extracts, others showed only the color of sulfur in xylene. The results obtained from several blacks follow in Table V.

**Table V—Reaction Products as Shown by Extract**

| Black | Time of Heating *Hours* | Color of Extract |
|---|---|---|
| Micronex | 4 | Dark reddish brown |
| Cabot | 8 | Reddish brown |
| Goodwin | 4 | Pale yellow |
| Activated Micronex | 4 | Very dark red-brown |
| Acetylene | 4 | Red-brown |

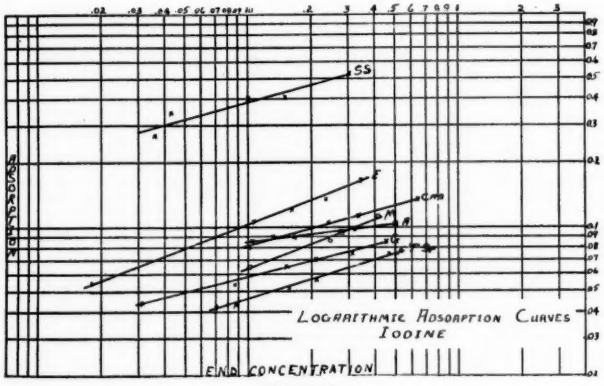


**Figure 3**

From the fact that only a pale yellow extract was obtained when sulfur, zinc oxide, or black was omitted or when the black was extracted alone, it seems that a reaction of the three took place, liberating an absorbed hydrocarbon which probably reacted with part of the sulfur. On concentrating the extract most of the sulfur crystallized out in needles and was removed. Removal of all the solvent left a gummy resin which still contained 77 per cent total sulfur. This resin, when compounded in an unaccelerated stock (allowance made for sulfur in the resin), shortened the time of cure from 2 hours to $1^1/_2$ hours at 141° C. and gave a somewhat stiffer stock. The experiment was repeated with acetylene black and a similar result was noted.

This experiment is proof of a peculiarity in rate of cure noted in the writers' laboratories and best expressed in tabular form (Table VI).

Table VI—Effect of Zinc Oxide and of Black on Rate of Cure

| Rubber | Sulfur | ZnO | Black | Time of Best Cure at 141° C. |
|---|---|---|---|---|
| *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Minutes* |
| 100 | 10 | .. | .. | 150 |
| 100 | 10 | 5 | .. | 150 |
| 100 | 10 | .. | 36 | 180 |
| 100 | 10 | 5 | 36 | 120 |

The addition of black to a rubber-sulfur mix slows down the time of cure, but the addition of black to a rubber–sulfur–zinc oxide mix accelerates, evidently owing to the liberation of an accelerator.

No change in iodine adsorption or in rate of cure in a Captax stock was found in the black from which the material was extracted. Its amount was very small, perhaps 0.25 per cent of the black. Black which had been boiled with sulfur and zinc oxide in xylene for several days retained about 1.0 per

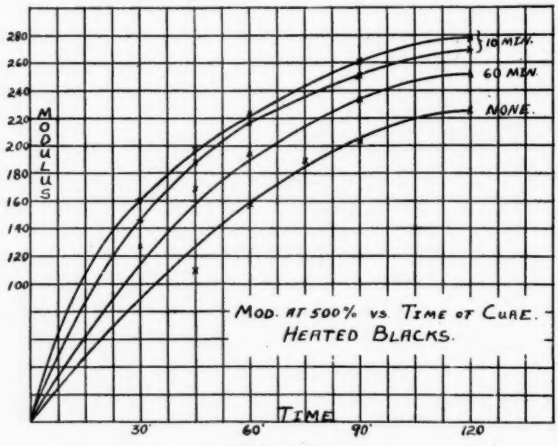


Figure 4

cent sulfur after repeated extractions with benzene, carbon disulfide, and finally 16 hours with acetone. While boiling in xylene, large quantities of hydrogen sulfide were evolved, probably due to the same reaction by which hydrogen sulfide is formed when paraffin and sulfur are heated together.

Another experiment was made which shows the strong adsorptive power of black for sulfur. A channel black and sulfur were heated in the activation apparatus for 2 hours at 540–590° C. A large amount of sulfur dioxide was evolved but after repeated and continuous extraction with carbon disulfide and finally with acetone, the black still contained 7 per cent adsorbed sulfur.

### Rate of Settling

A series of experiments on rate of settling was undertaken in an attempt to show some relation between this property and the action of the blacks in a rubber mix. One gram of

black was ground in 2.5 grams of linseed oil on a glass plate. This paste was then diluted with benzene and, after shaking out all lumps, was allowed to settle in a stoppered test tube. The data showed a large difference between blacks but was not related to any physical quality of the black-rubber mix.

Stamberger investigated the action of various materials in rubber cements, especially their rate of settling. If we suppose that in a mixture of black and rubber in benzene, certain blacks are able to bind themselves more firmly to rubber than others, owing to fineness of subdivision, deflocculation, or degree of dispersion, then some quantitative measurement should give us an indication of the quality of the black-rubber mix. Such a measurement is found in the actual determination of carbon in suspension in a 0.5 per cent rubber cement after centrifuging. One gram of black was ground into a paste with toluene or xylene on a glass plate. A few cubic centimeters of 4 per cent rubber cement were added and the grinding continued until the black and rubber were thoroughly mixed. The paste was then transferred to a bottle containing 50 cc. of 4 per cent rubber cement and all lumps were broken up. The cement was then gradually diluted to 400 cc. with benzene, with constant stirring, and was then uniform and free from lumps. The bottle was placed in a shaking machine for an hour or shaken by hand occasionally over an 8-hour period. The solution was then allowed to settle overnight or for 24 hours or a portion of it was centrifuged for 15 to 30 minutes. The supernatant liquid was analyzed for carbon by evaporating off the solvent on the steam bath, dissolving the rubber in cold concentrated nitric acid (preferably overnight), then heating to boiling, and filtering hot through a Gooch crucible packed with acid-washed asbestos.

By this means it was found possible, not only to differentiate between blacks made by different processes, but also to classify blacks from the same source as to their value in a rubber mix. In practically all cases a high-modulus black showed a high carbon-in-suspension figure. The test applied only to stiffness as determined by modulus in the standard test formula and was not a measure of hardness or plasticity of the uncured stock. Table VII is a comparison of modulus with amount of carbon held in suspension after 30 minutes' centrifuging.

**Table VII—Comparison of Modulus with Rate of Settling**

| Black | Carbon in Suspension | Modulus at 500% |
|---|---|---|
| | *Gram/100 cc.* | *Kg./sq. cm.* |
| Thermatomic regular | 0 | 110 |
| Thermatomic special | 0 | 110 |
| Super-Spectra | 0.011 | 160 |
| Micronex, low-quality | 0.0095 | 125 |
| Micronex, medium-quality | 0.026 | 160 |
| Micronex, high-quality | 0.035 | 194 |
| Experimental black | 0.062 | 186 |
| Goodwin | 0.055 | 207 |
| Acetylene | 0.067 | 210 |

There is overlapping of figures for different groups, but in general Thermatomic carbons have no affinity for rubber,

zero carbon being held in suspension; paint or varnish blacks will be less than 0.020 gram; channel blacks run between 0.02 and 0.04 gram, except the poor ones which will run lower; thermal decomposition blacks will run over 0.050 gram per 100 cc. cement. Rate of settling and degree of dispersion after centrifuging are different phenomena, as there was no relation between settling experiments and dispersion results. Regular Thermatomic and Super-Spectra are highly dispersed in linseed oil–benzene but are not retained in suspension by a rubber cement.

It is possible to distinguish between high- and low-quality blacks from the same shipment by this method, as a difference of 10 kg. in modulus will show up in amount of carbon held in suspension. The modulus at 500 per cent of several different samples of Micronex was determined in the standard test formula and compared with the amount of carbon held in suspension. It will be seen that the amount of carbon decreases with a decrease in modulus.

**Table VIII—Comparison of Blacks from Same Shipment**

| Lot | Carbon in Suspension | Modulus at 500% |
|---|---|---|
| | *Gram/100 cc.* | *Kg./sq. cm.* |
| 54 | 0.0195 | 200 |
| 59 | 0.016 | 193 |
| 56 | 0.014 | 190 |
| 55 | 0.013 | 183 |
| 53 | 0.012 | 178 |

The figures in Table VIII are not isolated instances, but have been noted in several series. It is of interest that the first four blacks listed would be classified as high-quality by Johnson's volatile matter test while the fifth would be low-quality.

*Note*—The figures for grams of carbon in suspension in Table VIII are somewhat lower than figures obtained for the same kind and quality of black and shown in Table VII, since a somewhat thinner rubber cement was used in the second series. To be comparable, all tests must be run on a cement made from one batch of rubber and over a period of 3 or 4 days, since a rubber cement in benzene does not maintain the same viscosity or rubber content indefinitely.

The union of black and rubber is a powerful forc e as is shown by the fact that high-quality blacks cannot be totally centrifuged from a rubber cement even by further dilution. This is true of no other pigment.

When a black is milled into rubber, the union is still more difficult to break by centrifuging. The difference between blacks is still observed, but the scale is narrower. Other pigments when milled into rubber can be centrifuged out.

The accuracy of the test is remarkable when we consider that the quality of the black may be determined by 1 to 5 per cent of the weight of sample taken, and yet we have seldom found a black that could not be classified as to modulus in the cured stock by this method.

## Acknowledgment

Thanks are due to R. P. Dinsmore for permission to publish this paper, to C. R. Park and C. R. Johnson for helpful criti-

cism, and to the Godfrey L. Cabot Company and to Binney & Smith for samples of carbon black.

## Literature Cited

(1) Bartell and Miller, *J. Am. Chem. Soc.*, **45**, 1106 (1923).
(2) Beaver and Keller, IND. ENG. CHEM., **20**, 817 (1928).
(3) Davis, *J. Chem. Soc.*, **91**, II, 1666 (1907).
(4) Goodwin and Park, IND. ENG. CHEM., **20**, 706 (1928).
(5) Johnson, *Ibid.*, **20**, 904 (1928).
(6) Leblanc, Kroeger, and Kloz, *Kolloidchem. Beihefte*, **20**, 356 (1925); *C. A.*, **19**, 3398 (1925).
(7) Spear and Moore, IND. ENG. CHEM., **18**, 418 (1926).
(8) Stamberger, *Kolloid-Z.*, **42**, 295 (1927).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 12, page 1288. December, 1929.]

# Carbon Black

## II—The Role of Oxygen[1]

C. R. Johnson

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**The results reported in this paper confirm the indication of previous work that a portion of the oxygen in carbon black exists in rather definite chemical combinations on the surface of a hydrocarbon with a high carbon-hydrogen ratio. It is not clear yet whether all of the oxygen in carbon black exists in this state, as previous work has shown that after heating for extended periods at 955° C. there still remains a small amount of oxygen in the black. It has been shown that the oxygen attached as here described does not exist in the state of gaseous adsorption and cannot be removed by heat alone as oxygen, but can be removed by reaction with zinc dust at temperatures below that at which gaseous evolution usually takes place. The oxygen goes over to zinc oxide and the volatile matter of the residue is considerably reduced.**

**No correlation between volatile matter (oxygen content) and iodine adsorption could be found, but a comparison of blacks from any one factory with respect to iodine adsorption shows that high iodine values follow high volatile matter content. Using two accelerators, it was found that the so-called high volatile blacks, which retard cure, adsorb more organic accelerators than a normal black. Those blacks which have been heated after manufacture at temperatures between 500° and 900° C. invariably show high iodine adsorption and lower accelerator adsorption, which accounts for their much more rapid vulcanization rate. Just why the iodine adsorption values are inconsistent with other phenomena is not clear at present. An explanation of poorer physical tests in rubber with high volatile blacks is given. The development of a**

[1] Presented before the Rubber Division of the American Chemical Society, at Atlantic City, N. J., September 26 to 28, 1929.

**new carbon black with low accelerator adsorption and improved physical properties when used with rubber is included.**

THE phenomenon of adsorption and the status of oxygen in carbon black are very closely related. Any addition to our knowledge of this relationship will help to explain the properties of carbon black in its use with rubber, as well as in inks and varnishes. At several different periods the adsorptive properties of carbon black have been studied. Spear and Moore (*7*) showed that the adsorption of different carbon blacks for organic dyes was variable and found some correspondence between the oil adsorption properties of the several blacks and their behavior in rubber. Beaver and Keller (*2*) studied the iodine adsorption of carbon blacks in connection with their work on the influence of oxygen on the properties of carbon black. Goodwin and Park (*3*), in their complete work on the physical and chemical properties of carbon blacks and their relationship to the properties when used in rubber, emphasized the importance of adsorption.

Sebrell and Carson (*6*) showed that the rate of cure of different blacks in rubber was roughly inversely as the iodine adsorption of the several blacks which were studied. They showed also that the black had the capacity to adsorb organic accelerators. In one instance, however, he reported an inconsistency which was difficult to explain. When a carbon black was heated to about 800° C. for a short period the adsorptive capacity was materially increased and at the same time the rate of cure in rubber was notably increased. Sebrell and Carson's work is responsible in part for the work reported in this paper, as a number of points in their report were stimulative of further study.

It has been shown (*4*) that oxygen is important in its bearing on the behavior of carbon black in rubber. While oxygen was revealed in an ultimate organic combustion of carbon black, whenever carbon black was heated to temperatures above 400° C. gas evolution took place, the gases evolved consisting principally of hydrogen, carbon monoxide, carbon dioxide, and a very small percentage of oxygen. This result is in conformity with Langmuir's findings (*5*) that whenever oxygen is adsorbed on the surface of a carbon lamp filament the oxygen cannot be driven off as such by heating, but takes carbon atoms with it in the form of carbon monoxide and carbon dioxide. It is Langmuir's concept that the oxygen in this case is combined on the surface of the carbon in a little more definite chemical combination than is usual in adsorption, and that the surface is covered with a monomolecular layer of oxygen with primary valences attached to the carbon. It was shown by several experiments that the same rule probably held with respect to carbon black. One of these was the determination of the volatile matter of carbon black at 2 mm. pressure in comparison with the same determination

made at atmospheric pressure. In all cases the volatile matter at low pressure was less than at higher pressure, and the explanation which was suggested was that the oxygen was removed at low pressure without combining with the carbon, thus making a lower volatile loss. This was supported by the fact that an analysis of the gases evolved when that black was heated *in vacuo* showed more hydrogen, more oxygen, and less carbon monoxide and carbon dioxide.

It was the purpose of the investigation discussed in this paper to more definitely fix the status of oxygen and to find what influence, if any, it has on the properties of black when used in rubber.

### Effect of Oxygen on Carbon Black

According to Freundlich (*1*), in the case of true gaseous adsorption there exists an exact equilibrium between the amount of gas adsorbed on a surface and the concentration of the same gas in contact with that surface. Such being the case, if oxygen be present as a truly adsorbed gas on carbon black, then the concentration of adsorbed oxygen should be diminished if black be placed in an oxygen-free atmosphere. A sample of black was placed in an atmosphere of nitrogen, and after each 24 hours a portion of the sample was removed for volatile matter determination. At the same time the nitrogen atmosphere was renewed. It had already been determined that for all of the blacks used in rubber there was a definite ratio between the oxygen content and the volatile matter content, which averages 0.863. Table I shows that there is no diminution of oxygen as a result of exposure to pure nitrogen.

**Table I**

| Period in Nitrogen | Volatile Matter |
|---|---|
| *Days* | *Per cent* |
| Start | 5.75 |
| 1 | 5.63 |
| 2 | 5.84 |
| 4 | 5.90 |
| 7 | 5.79 |
| 9 | 5.77 |
| 13 | 5.76 |

The objection might be raised that the data in Table I are not conclusive because after exposure to nitrogen the black, for a short period, is exposed to the atmosphere and possibly could take on oxygen again before the volatile matter determination was made. As a check on this point another test was run in which the black was soaked in nitrogen gas in a quartz tube for 2 days. The volatile matter determination was made directly in the quartz tube without exposing it to the atmosphere. The same sample of black was used as in making the determinations reported in Table I. The volatile matter decreased from 5.80 per cent at the start to 5.72 per cent after 2 days in nitrogen. From this it can reasonably be assumed that the oxygen content of carbon black is in a more definite chemical relationship to the carbon than strictly gaseous adsorption.

Another experiment was made to determine whether or not the carbon black could be made to take on oxygen in a strong oxygen concentration. A sample was exposed to a sample of liquid air containing 50 per cent oxygen for 15 minutes and for 6 hours, with the results shown in Table II.

**Table II**

| Treatment of Sample | Volatile Matter after Exposure for 15 minutes | 6 hours |
|---|---|---|
| | *Per cent* | *Per cent* |
| Before exposure | 3.99 | 3.99 |
| After exposure | 4.20 | 4.31 |
| After exposure and 20 hours in air | 4.07 | 4.26 |
| After exposure and 68 hours in air | .. | 4.18 |

It would appear from the results in Table II that carbon black is not completely saturated with respect to oxygen, and that if oxygen is added it is in fairly stable condition, as the volatile matter loss is only slightly reduced after long exposure to air after the black has been in liquid oxygen for 6 hours.

Another study was made to throw more light on the possibility of the addition of oxygen. It had been observed that when carbon black was heated in the presence of air sometimes oxygen was added and sometimes it was removed from the carbon black. As a general rule, oxygen was removed at temperatures above 500° C. and added at temperatures below 450° C. Two runs were made as follows:

Test 1—Heated for 5 minutes at 90–150° C., passing air over crucible placed in electric muffle furnace. Removed to desiccator and weighed. Volatile matter determined.

Test 2—Heated for 5 minutes at 275–325° C. Other conditions the same as in Test 1.

The results of these two tests are given in Table III.

**Table III**[a]

| | Before Heating | | | | After Heating | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature | Loss on heating | Volatile loss | Moisture | Net volatile loss | Volatile loss | Moisture | Net volatile loss | Carbon loss | Gain in volatile |
| ° C. | % | % | % | % | % | % | % | % | % |
| 90 to 150 | 8.52 | 6.45 | 1.16 | 5.29 | 5.99 | 0.47 | 5.52 | 0.37 | 0.18 |
| 275 to 325 | 7.96 | 6.45 | 1.16 | 5.29 | 6.09 | 0.45 | 5.64 | 0.37 | 0.30 |

[a] It was assumed that the net change in carbon could be represented by the weight of the residue after each volatile matter determination. This is substantially correct, except for a small amount of hydrogen in the residue.

The results of these two tests indicate that whenever equilibrium conditions are favorable for the addition of oxygen it takes place, and that the loss in carbon calculated from volatile matter residues is about equal to the gain in volatile matter after heating to temperatures of 90–325° C. in the presence of air. According to an equation derived by Duerr, the gain in volatile matter should be about 2 to 3 times the loss in carbon, thus:

$$W'V' - WV = 7 \text{ to } 11 \times \frac{(W - WV - W' - W'V')}{3}$$

where $W$ = dry weight of original sample
$W'$ = dry weight after increasing oxygen content
$V$ = volatile matter before heating
$V'$ = volatile matter after heating

The factor $\frac{7 \text{ to } 11}{3}$ takes into account the fact that the oxygen comes off as a mixture of CO and $CO_2$.

The ratio of the gain in volatile matter to the loss in carbon is less than 1 and does not conform to the expectations of the equation, but the difference can be explained by the fact that there is a greater loss in weight during heating than can be accounted for by the difference in the moisture before and after heating. Apparently some volatile matter loss takes place even at the low temperature of heating, and while the black was being oxidized and increasing in its volatile matter capacity there was a definite carbon loss.

Having shown that it is possible to add oxygen to carbon black, it is now advisable to consider the possibility of removing it. It has already been shown (*4*) that it is possible to remove it in part by heating in the absence of air at temperatures above 500° C. The experiment was tried by treating the carbon black with a powerful reducing agent, zinc dust being chosen as the reagent. An intimate mixture of 20 per cent zinc dust and 80 per cent Cabot's black from the Bowers plant was treated as follows: (1) heated 1 hour under vacuum at 370° to 400° C.; (2) heated 2 hours under vacuum at 370° to 400° C.; (3) mixture (enough for rubber test) heated 1½ hours under vacuum at 370° to 400° C. The gain in weight after heating was 0.158 per cent in Test 1 and 0.135 per cent in Test 2. The volatile matter run under vacuum at 800° C. for 7 minutes was, in Test 1: carbon black (without zinc dust), 3.23 per cent; unheated mixture, 0.85 per cent; heated mixture, 0.92 per cent. In Test 2 it was: heated mixture, 0.54 per cent. In Test 3 it was: unheated mixture, 1.04 per cent; heated mixture, 0.89 per cent.

The results of the rubber test[2] on the original black and on the heated mixture are given in Table IV.

**Table IV**

| Period of Cure | Tensile at Break | | Elongation at Break | Modulus at 400% Elongation | Hardness Shore Durometer |
|---|---|---|---|---|---|
| *Minutes* | *Lbs. per sq. in.* | *Kg. per sq. cm.* | *Per cent* | | |
| | | ORIGINAL BLACK | | | |
| 40 | 4035 | 284.2 | 640 | 1710 | 62 |
| 60 | 4100 | 288.7 | 623 | 2060 | 65 |
| 80 | 4250 | 299.3 | 603 | 2265 | 68 |
| | | HEATED MIXTURE | | | |
| 40 | 3830 | 269.7 | 617 | 1750 | 62 |
| 60 | 3900 | 274.6 | 567 | 2180 | 67 |
| 80 | 4025 | 283.4 | 580 | 2130 | 68 |

A mixture of 20 per cent zinc dust and 80 per cent Cabot's black from the Bowers plant was heated for 4½ hours at 400° C. After 1½ hours the apparatus was disconnected, a small sample was removed, and the mixture was stirred, after which heating was resumed under vacuum.

The volatile matter in the mixture run under vacuum at

[2] In testing the heated mixture, it was assumed that the zinc dust had changed to zinc oxide and correction was made in the test formula.

800° C. for 7 minutes and the adsorption of 0.1 *N* iodine by the mixture are shown in Table V.

**Table V**

| | Volatile Matter | Iodine per Gram Black |
|---|---|---|
| | *Per cent* | *Grams* |
| Carbon black (without zinc dust) | 3.15 | 0.130 |
| Zinc dust | .. | 3.627 |
| Zinc oxide | .. | None |
| Unheated mixture | 1.34 | 0.715 |
| Heated mixture (1½ hours) | .. | 0.419 |
| Heated mixture (4½ hours) | 2.26 | 0.376 |
| Heated mixture (4½ hours) exposed to air for 3 days | 2.06 | ... |

The combustion analyses are shown in Table VI.

**Table VI**

| | Heated Mixture | Original Black |
|---|---|---|
| | *Per cent* | *Per cent* |
| Carbon | 77.28 | 93.18 |
| Hydrogen | 1.35 | 1.06 |
| Oxygen | 1.77 | 5.76 |
| Ash | 19.60 | None |
| Moisture | 0.67 | 1.20 |

From the data in Tables V and VI it is evident that the volatile matter is considerably reduced even before the mixture is heated, which shows that the oxygen has been removed from combination with the carbon and has reacted with the zinc dust to form zinc oxide in the process of volatile matter determination. In the case of the iodine adsorption, the amount found on the unheated mixture is almost exactly 20 per cent of the amount for pure zinc dust, so that practically no iodine goes to the black in that instance. With the heated mixture, the iodine adsorption falls off, owing to the fact that some of the zinc dust has gone over to the oxide, which has no adsorptive capacity for iodine.

It might be argued that the zinc oxide is formed by reaction of the zinc with the carbon dioxide, rather than directly with the oxygen. From a consideration of heats of formation, the facts that ordinarily gases are not evolved from carbon black at temperatures as low as that used, that there was no appreciable loss in weight in the heated mixture, and that there was no appreciable gas evolution during heating indicate that this reaction involves the taking of oxygen from the carbon by the zinc, without the intermediate formation of carbon dioxide.

The next step appears to be to try the reducing effect of hydrogen at various temperatures and pressures. If hydrogen is effective, it might have a practical as well as a theoretical interest, from the possibility of changing the properties of carbon black in its various uses. At any rate, it can now be asserted that the oxygen of carbon black is not so firmly attached to the carbon that it cannot be removed without appearing as carbon monoxide or dioxide.

### Adsorption Phenomena

Sebrell and Carson's work on iodine adsorption was concerned with blacks produced by different processes, and there

Table VII

| Sample | Quality | Treatment | Volatile | Iodine Absobed Per Gram Black (Dry) from: 0.05 *N* I | 0.1 *N* I | 0.2 *N* I | Captax | DPG |
|---|---|---|---|---|---|---|---|---|
| | | | *Per cent* | *Gram* | *Gram* | *Gram* | *Gram* | *Gram* |
| Schafer 1654 | Good | | 5.48 | 0.136 | 0 149 | 0.166 | 0.0317 | 0.0237 |
| Schafer 1691 | Poor | | 7.35 | 0.158 | 0.171 | 0.211 | 0.0400 | 0.0524 |
| T Elf 199 | Good | | 5.13 | ... | 0.104 | ... | 0.0284 | .... |
| T Elf 16 | Poor | | 6.67 | ... | 0.138 | ... | 0.0377 | .... |
| Schafer 1078 | | Original | 5.02 | ... | ... | ... | 0.0266 | 0.0183 |
| Schafer 1078 | | Heated 2 hours at 650° C. | 2.80 | ... | ... | ... | 0.0231 | 0.0150 |
| Schafer 1691 | | "As is" | 7 35 | 0.153 | 0 171 | 0.211 | .... | .... |
| | | Heated 5 minutes at 650° C. | 6.82 | 0.161 | 0.178 | 0.202 | .... | .... |
| | | Heated 20 minutes at 650° C. | 5.09 | 0 202 | 0.223 | 0.230 | .... | .... |
| Schafer 1078 | | "As is" | 5.02 | 0.126 | 0.146 | 0.160 | .... | .... |
| | | Heated 120 minutes at 650° C. | 2 80 | 0.183 | 0.195 | 0.204 | .... | .... |
| Schafer 1654 | Good | | 5 48 | ... | 0.149 | ... | .... | .... |
| Schafer 1078 | Good | | 5 02 | ... | 0.146 | ... | .... | .... |
| Schafer 1692 | Good | | 5 36 | ... | 0.138 | ... | .... | .... |
| Kingsmil 1823 | Good | | 3 99 | ... | 0.138 | ... | .... | .... |
| Powers 1821 | Good | | 5 67 | ... | 0.143 | ... | .... | .... |
| T Elf 199 | Good | | 5.13 | ... | 0.104 | ... | .... | .... |

is some question as to whether or not it is safe to generalize from data under such conditions. It was deemed advisable to study the adsorption of iodine and some organic accelerators by rubber blacks which were known to vary widely in the volatile matter content, and consequently in the rate of vulcanization of rubber. The data in Table VII show, in the case of unheated blacks, that there is no correlation between iodine adsorption and the amount of volatile matter in black, or in the rate of cure of the black when used with rubber. When samples of black from the same factory are considered, however, it is usual to find that the iodine adsorption varies directly with changes in volatile content. Studies of adsorption of two accelerators, Captax and DPG, by a number of blacks indicate that accelerator adsorption varies directly with volatile matter (oxygen content). This applies not only to samples from a given factory but throughout a number of sources. The exception which Sebrell and Carson noted with heated blacks, namely, that iodine adsorption was increased and volatile matter decreased, accompanied by more rapid curing rate, is confirmed by the data in Table VII.

Taking the ideas developed in this and other papers, it begins to be clear now why carbon black with high volatile matter (or oxygen content) gives poor physical properties when vulcanized with rubber. Such black clearly has the property of adsorbing more organic accelerator than a normal black, with the result that there are established innumerable foci of incompletely vulcanized points throughout the rubber mixture caused by the conjuncture of a black particle, rubber nucleus, sulfur particle, and reduced accelerator concentration. This leads to a reduced average strength throughout the mass, and consequently lower tensile and lower modulus. The lower rate of cure is clearly explained by the reduction in accelerator concentration. For over two years the writer has been studying the possibilities of overcoming the phenomenon of accelerator adsorption. The investigations here reported have been favorable, and concurrent examination of the new product by several rubber manufacturing companies has demonstrated that carbon black in which accelerator adsorption is largely inhibited can be made. Extensive tests over a period of 8 months in a large manufacturing laboratory have indicated that this new black has physical properties 20 per cent better than normal channel black. Test tires are now on the road to confirm the preliminary abrasion results.

## Acknowledgment

Acknowledgment is due W. A. Duerr for the scheme followed in studying the addition and removal of oxygen at various temperatures. Acknowledgment is also due H. P. Gurney, R. K. Estelow, and Jacob Gabry for assistance in the preparation of this paper.

## Literature Cited

(1) Alexander, "Colloid Chemistry," Freundlich, p. 575.
(2) Beaver and Keller, IND. ENG. CHEM., **20**, 817 (1928).
(3) Goodwin and Park, *Ibid.*, **20**, 706 (1928).
(4) Johnson, *Ibid.*, **20**, 904 (1928).
(5) Langmuir, *J. Am. Chem. Soc.*, **37**, 1154 (1915).
(6) Sebrell and Carson, IND. ENG. CHEM., **21**, 911 (1929).
(7) Spear and Moore, *Ibid.*, **18**, 418 (1926).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 12, page 1183. December, 1929.]

# The Aging of Vulcanized Rubber under Varying Elongation[1]

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IT IS well known that a piece of rubber tubing cracks at that point where it is stretched over a metal nipple, or a piece of water hose cracks where it is stretched over a nozzle. Figure 1 illustrates the cracking of natural-aged rubber goods at those parts which are under some degree of tension or strain. Inasmuch as rubber does crack or deteriorate faster when stretched, experimental work was contemplated to determine the relative degree or rate of deterioration at different percentages of stretch or elongation.

## Experimental Method

Circular test rings were cut from flat sheets of cured rubber, then stretched and held at different elongations on a stepped steel cone. (Figure 2) The sizes of the steps on this cone are such that the test rings are stretched from 0 to 100 per cent. Straight mandrels of varying size were also used in addition to this stepped cone. Aging of the rings on the stepped cone or on the mandrels was then done under four conditions: (1) in the Geer oven where the principal factor concerned is heat; (2) in the Bierer-Davis bomb where the chief factor is oxygen; (3) in an electric spark chamber where the principal factor is ozone; and (4) in the great outdoors where the chief factor is sunlight.

It should be definitely understood that this experimental work concerns itself only with static aging, not with dynamic aging where the test strip is being twisted, flexed, bent, or stretched repeatedly during the aging process. That problem of dynamic aging is entirely different from the present problem

[1] Presented before the meeting of the Division of Rubber Chemistry of the American Chemical Society, Atlantic City, N. J., September 26, 1929.

of static aging at different elongations, particularly when waxy materials are used in the compound to form a protective film.

A total of sixty-six compounds or recipes was used. These compounds were first cured in sheet form in molds, a range of cures was made at one temperature, tensiles were determined

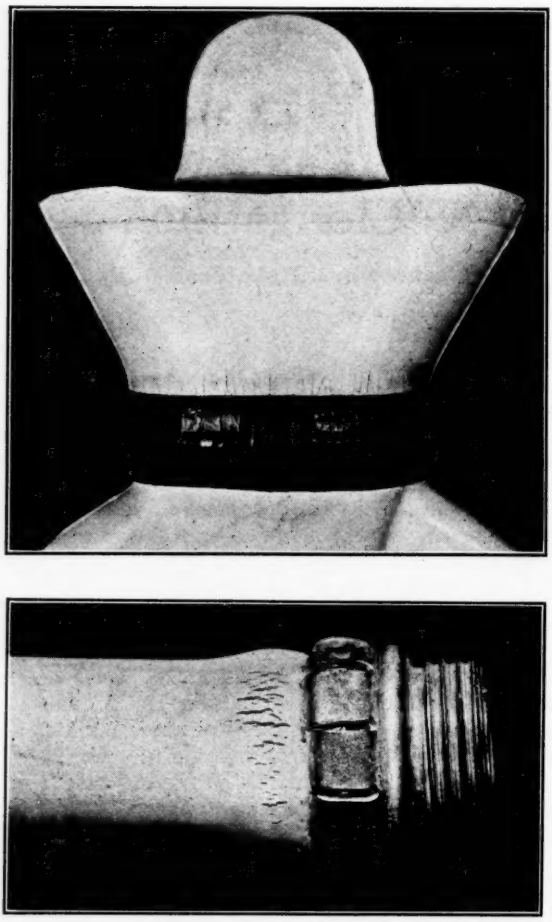

**Figure 1—Natural-Aged Rubber Cracked at Parts under Tension**

on dumbbell test strips, and what was deemed to be the proper cure or cures was determined from the tensile-time curve. (Figure 3) This curve has been shown before, and simply represents tensile strength plotted against time of cure. From it the point or points which are considered the proper cures are chosen.

**Factors Studied**

The variation in the rate and degree of deterioration with respect to varying elongation was then studied as affected by the following factors: (1) fillers; (2) volume loadings; (3) accelerators; (4) percentages of accelerators; (5) percentages

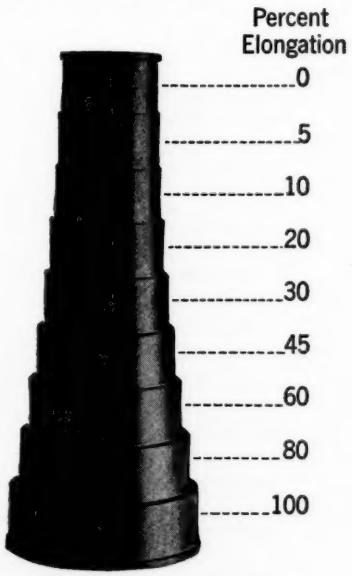


**Figure 2—Stepped Cone**

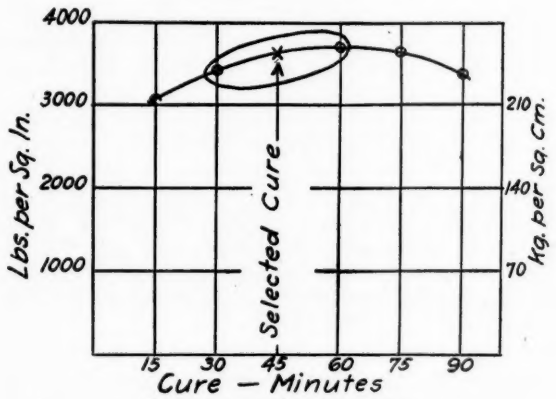


**Figure 3—Tensile-Time Curve**

of sulfur; (6) antioxidants; (7) percentages of antioxidants; (8) softeners and waxes; (9) vulcanizing agents; (10) percentages of vulcanizing agents; (11) rubbers, including synthetic; (12) times of cure; (13) periods of bomb aging.

The formula for the basic control compound used for the

greater amount of the work was made about as simple as possible, and is as follows:

| | *Parts* |
|---|---|
| Rubber | 100 |
| Zinc oxide | 5 |
| Gilders whiting | 60 |
| Stearic acid | 1 |
| Sulfur | 4 |
| Diphenylguanidine | 1.25 |

Cure: 10, 15, 30, 45, 60 minutes at 2.8 kg. per sq. cm. (40 lbs. per sq. in.)

In addition to the above, aging tests were made on rubber bands at different elongations from 0 to 700 per cent. These bands were pure gum with 5 or 6 per cent sulfur plus antioxidant.

## Results

Figure 4 shows an average or composite curve of all these sixty-six compounds aged for one period of time (12 days) at nine different elongations in an oven. Each point on this curve, for instance at 100 per cent elongation, consists of an average of the tensiles of sixty-six different compounds; all of these compounds aged for 12 days in the oven at 100 per cent elongation, then broken, tensile strengths determined, and the average taken for that point, and similarly for all the other points. This composite curve shows that in oven aging deterioration is approximately 30 per cent greater when the sample is stretched 100 per cent than when it is stretched 0 per cent. Figure 5 shows an analogous composite curve for the same sixty-six compounds aged under similar conditions of stretch one period of time (24 hours) in the bomb. This curve indicates that aging in the bomb is almost independent of the amount the sample is stretched. Figure 6 shows the composite or average curve for the same sixty-six compounds aged one period of time (45 minutes, concentration unknown) in ozone. The ozone chamber or closet contains several pairs of metal plates at a difference of potential of 20,000 volts. The rubber test rings are placed about these plates and the ozone is distributed by means of an electric fan. It will be noted that this curve is not a straight line, but has a dip in it. Figure 7 shows a composite curve for the same sixty-six compounds aged in sunlight one period of time (17 days) the latter part of August and the first few days of September, and there was real sunlight all that period. Here again there is a dip in that curve.

From these curves it can be concluded that it is not heat and it is not oxygen that causes a rubber to crack at a point where it is stretched; it is ozone or something comparable to ozone in sunlight, and there is a critical percentage of stretch or elongation where that deterioration is greatest.

Figure 8 shows curves on the control stock containing whiting, aged at different elongations in oven, bomb, ozone, and sunlight.

Test rings crack when aged under tension in ozone or sun-

light. Figure 9 shows the test rings of one compound that has been aged at the different elongations on the stepped cone in ozone. In order to photograph these rings they have been taken off the stepped cone and stretched 100 per cent.

Figure 10 shows the aging curves in ozone and sunlight of a 40 per cent carbon-black stock—that is, 40 parts of carbon black on 100 parts of rubber, which is equivalent in volume to 60 parts of whiting. Tire manufacturers say that the

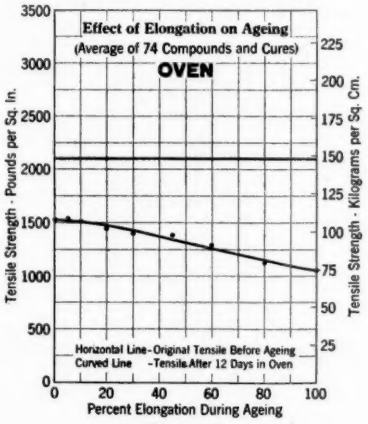


**Figure 4**

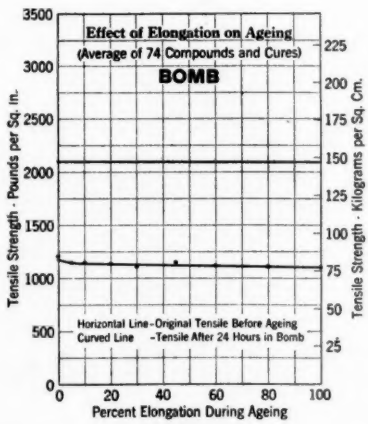


**Figure 5**

percentage of stretch in the side wall of a tire when it is inflated on a rim is from 6 to 12 per cent. It seems unfortunate that the critical point of this deterioration curve should come at about 10 per cent elongation.

As the sulfur is varied 2, 3, 4, and 5 per cent on the rubber, and the stocks are aged at different elongations, it appears that the deterioration increases as the sulfur is increased in either ozone or sunlight. (Figure 11)

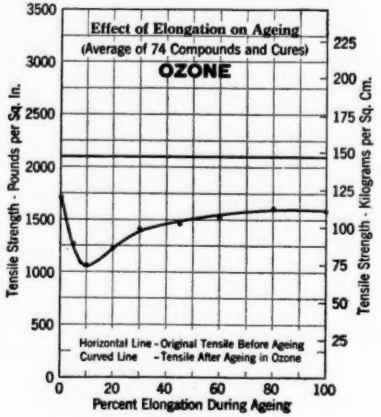
Effect of Elongation on Ageing
(Average of 74 Compounds and Cures)
OZONE
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Horizontal Line - Original Tensile Before Ageing
Curved Line - Tensile After Ageing in Ozone
Percent Elongation During Ageing

**Figure 6**

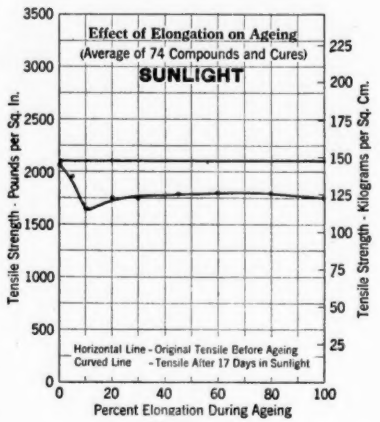
Effect of Elongation on Ageing
(Average of 74 Compounds and Cures)
SUNLIGHT
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Horizontal Line - Original Tensile Before Ageing
Curved Line - Tensile After 17 Days in Sunlight
Percent Elongation During Ageing

**Figure 7**

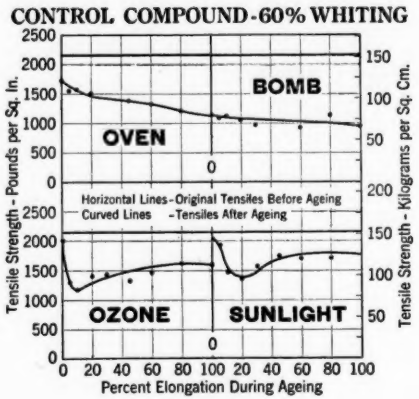
CONTROL COMPOUND - 60% WHITING
BOMB
OVEN
OZONE
SUNLIGHT
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Percent Elongation During Ageing

**Figure 8**

As the cure varies 10, 20, and 30 minutes, it appears that the under-cures deteriorate faster than the proper cure when aged in ozone or sunlight. (Figure 12)

As the loading of filler is varied 30, 60, 90, 120, and 150 parts of whiting on 100 parts of rubber, the percentage of deterioration at different elongations is not changed, and the dip in the curve when aging is done in ozone does not move along the horizontal axis. Figure 13 shows the aging of two of these different loadings in ozone as compared with the pure gum control containing no whiting.

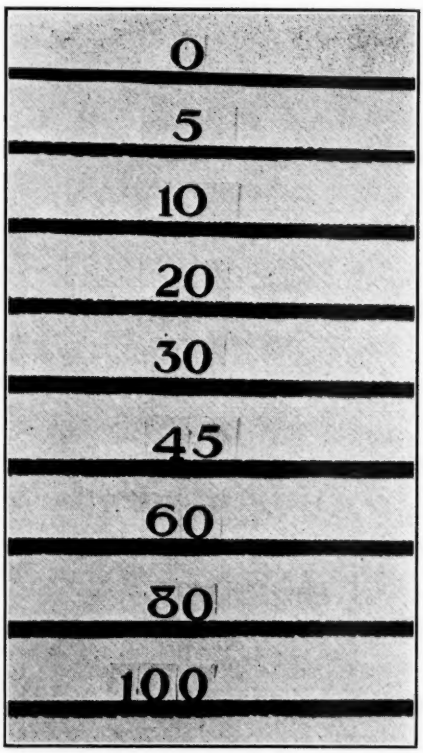


**Figure 9—Test Rings of Compound Aged at Different Elongations on Stepped Cone in Ozone**

The writers had ideas about correlating aging at various elongations with stress-strain data at very low elongations, and to this end have devised means for accurately determining stress-strains at low elongations—i. e., by molding a test ring or loop 25.4 cm. (10 inches) in length so that 25.4-cm. stretch on the testing machine is only 100 per cent elongation. The test ring or loop is of such cross section as to require a considerable pull to stretch it 100 per cent, and accordingly an accurate stress-strain curve can be drawn. That, how-

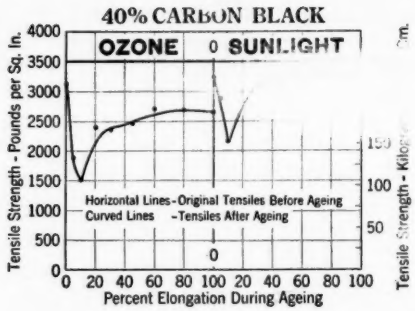
40% CARBON BLACK
OZONE
SUNLIGHT
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing
Percent Elongation During Ageing

**Figure 10**

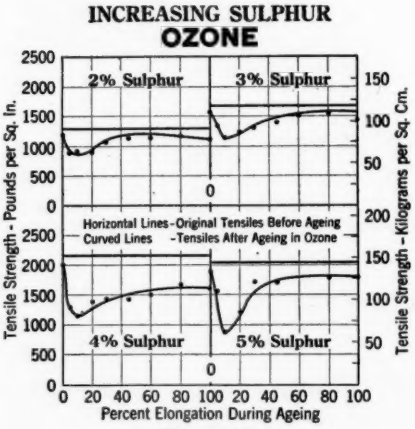
INCREASING SULPHUR
OZONE
2% Sulphur
3% Sulphur
4% Sulphur
5% Sulphur
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing in Ozone
Percent Elongation During Ageing

**Figure 11**

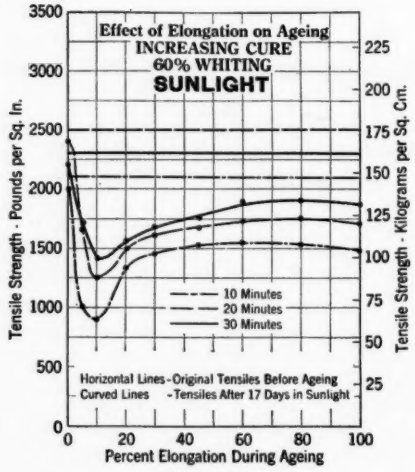
Effect of Elongation on Ageing
INCREASING CURE
60% WHITING
SUNLIGHT
10 Minutes
20 Minutes
30 Minutes
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After 17 Days in Sunlight
Percent Elongation During Ageing

**Figure 12**

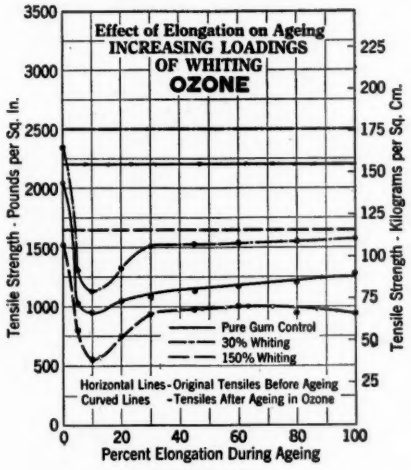
Effect of Elongation on Ageing
INCREASING LOADINGS
OF WHITING
OZONE
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Pure Gum Control
30% Whiting
150% Whiting
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing in Ozone
Percent Elongation During Ageing

**Figure 13**

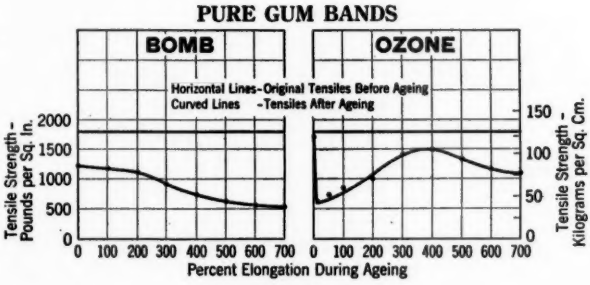
PURE GUM BANDS
BOMB
OZONE
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Percent Elongation During Ageing

**Figure 14**

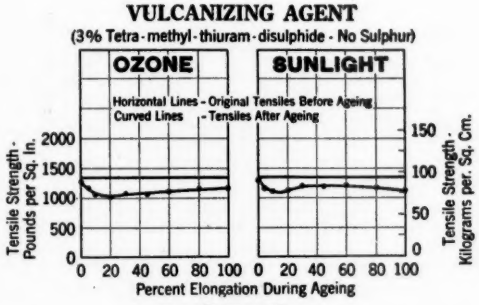
VULCANIZING AGENT
(3% Tetra-methyl-thiuram-disulphide - No Sulphur)
OZONE
SUNLIGHT
Horizontal Lines - Original Tensiles Before Ageing
Curved Lines - Tensiles After Ageing
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per. Sq. Cm.
Percent Elongation During Ageing

**Figure 15**

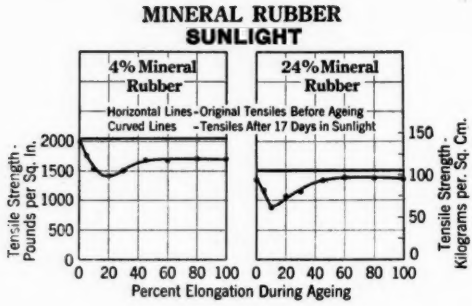


**Figure 16**

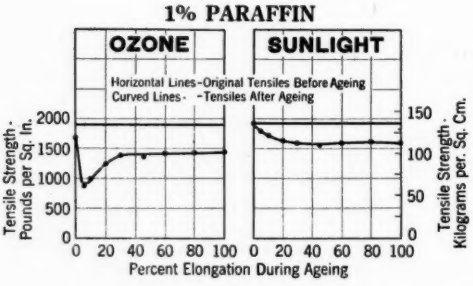


**Figure 17**

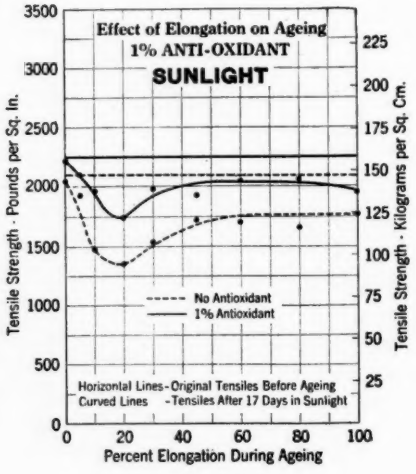


**Figure 18**

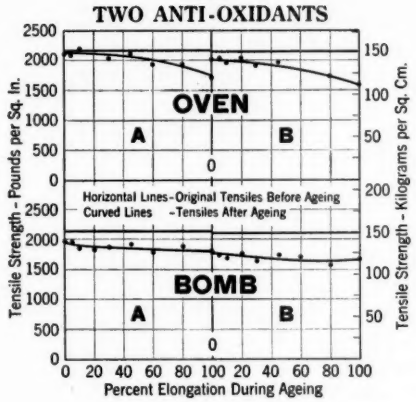


**Figure 19**

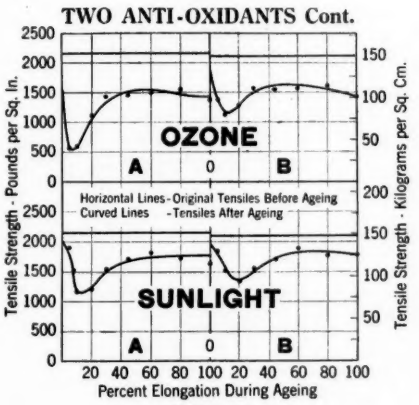


**Figure 20**

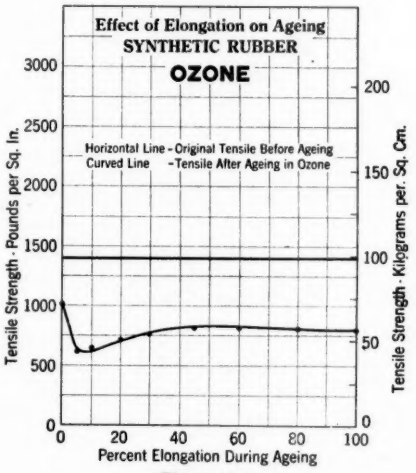
Effect of Elongation on Ageing
SYNTHETIC RUBBER
OZONE
Horizontal Line - Original Tensile Before Ageing
Curved Line - Tensile After Ageing in Ozone
Tensile Strength - Pounds per Sq. In.
Tensile Strength - Kilograms per Sq. Cm.
Percent Elongation During Ageing

**Figure 21**

ever, is another matter and has not as yet been tied up with the aging data at different elongations.

Figure 14 shows the aging curves for so-called pure-gum rubber bands aged in oxygen and ozone while they were stretched 0 to 700 per cent. That ozone curve has been duplicated and can be duplicated readily.

From the great amount of data obtained in this work, the results with certain vulcanizing agents show rather low percentages of deterioration during aging, and fairly flat aging curves in ozone and sunlight. Figure 15 shows the aging in ozone and sunlight of a compound cured with 3 per cent tetramethylthiuram disulfide as a vulcanizing agent without any added sulfur.

From the results on the series of compounds containing added softeners two sets of curves are shown—one for mineral rubber (Figure 16) and the other for paraffin (Figure 17). Although the two curves in Figure 16 are of about the same shape, the percentage deterioration is less if anything with the larger amount of mineral rubber, except at the critical elongation of about 10 per cent.

Paraffin is an interesting example of a material that causes bad deterioration in ozone but provides some protection in sunlight, and furthermore the sunlight curve does not have the characteristic dip at 10 per cent elongation. Possibly this might be explained by the protective film of paraffin breaking under stretch but uniting again during the period of sunlight aging when the weather was fairly hot.

The addition of an antioxidant does not change the shape of the sunlight- or ozone-aging curve—that is, it does not take that dip out of the curve at the 10 per cent elongation—but it may lessen the degree of deterioration. (Figure 18)

According to these four different methods of aging—heat, oxygen, ozone, and sunlight—different antioxidants do not always give comparable results. For instance, two antioxidants when tested in the oven, and the bomb may have a strictly comparable efficiency, as shown in Figure 19, whereas when tested in ozone and sunlight they may have an entirely different efficiency as shown in Figure 20.

Figure 21 shows the aging in ozone of a compound containing synthetic rubber. The tensiles are low inasmuch as the rubber had been lying in the laboratory nearly a year and had begun to oxidize, but the dip in the curve at 5 or 10 per cent elongation is still there.

### Summary of Results

1—Deterioration in the oven is approximately 30 per cent greater at 100 per cent elongation than at 0 per cent elongation.

2—Deterioration in the bomb is almost independent of elongation.

3—Deterioration in ozone is greatest at 5 and 10 per cent elongations.

4—Deterioration in sunlight with respect to stretch is analogous to deterioration in ozone.

5—Cracking of the test rings occurs in both ozone and sunlight when the rings are stretched, but not in the oven or bomb. This cracking is greatest at 5 and 10 per cent elongations.

6—A 40 per cent carbon-black stock shows marked deterioration and cracking in both ozone and sunlight at about 10 per cent elongation.

7—High sulfur causes greater deterioration in ozone and sunlight than low sulfur.

8—Undercures show greater deterioration than the optimum cure in ozone and sunlight.

9—Loading with a filler such as whiting does not change the shape of the ozone- and sunlight-aging curves, and does not materially affect the percentage deterioration.

10—Rubber bands show progres sively poorer aging in the bomb as the stretch increases from 0 to 700 per cent, while in ozone they give an aging curve having the characteristic dip at about 10 per cent elongation, showing the least deterioration at about 400 per cent elongation.

11—Tetramethylthiuram disulfide (3 per cent) as a vulcanizing agent causes rather low percentages of deterioration in ozone and sunlight, and gives fairly flat aging curves.

12—Mineral rubber (24 per cent) causes a smaller percentage deterioration than 4 per cent except at the critical elongation of about 10 per cent.

13—Paraffin (1 per cent) causes pretty bad deterioration in ozone but provides some protection in sunlight.

14—Added antioxidant does not change the shape of the ozone- or sunlight-aging curves but may lessen the amount of deterioration.

15—Two antioxidants may give comparable results in both oven and bomb, but quite different results in ozone and sunlight.

16—Synthetic rubber gives a characteristic ozone-aging curve.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1008. November, 1929.]

# Relation between Artificial Aging Tests and Natural Aging

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THE more varied the uses to which rubber is put, the more varied are the conditions under which it ages, and the less can it be expected that any single aging test will duplicate these various conditions. The most important factors which promote the deterioration of rubber goods are oxidation by atmospheric oxygen, after-vulcanization, heat effects, cracking and other changes from exposure to sunlight, and wear or deterioration due to mechanical work.

No two types of rubber products are exposed in just the same way to these various influences; in fact, one product may be exposed to a marked degree to only one of the influences whereas another may deteriorate from all five influences. Thus, automobile tires undergo oxidation, after-vulcanization, heat effects, cracking from exposure to sunlight and abrasion, and deterioration from mechanical work. On the other hand, steam hose tubes deteriorate predominantly from after-vulcanization and heat effects, oxidation, mechanical work and sunlight playing almost no part. After-vulcanization and oxidation are the most important factors in the deterioration of air-brake hose, while auto-topping and bathing caps undergo severe exposure to sunlight. In brief, each kind of rubber goods is exposed to different conditions, and to attempt to duplicate the different combinations of light, heat, oxygen, and mechanical work would lead to a different test for every type of rubber goods manufactured. Obviously, this is impracticable and undesirable.

The few artificial aging tests which have been developed up to the present time—including the Geer oven test, the Marzetti oxygen test, the oxygen bomb test, the ultra-violet light test, and the Fadeometer test, as well as numerous mechanical tests—have been based on the opposite principle; that is, to determine the resistance of a rubber product to the one most important influence to which it is exposed in

service. Thus, when bathing caps or auto-toppings are exposed to a Fadeometer or to ultra-violet light, the idea is only to intensify greatly the action of sunlight, while oxidation, after-vulcanization, and other effects are ignored. Similarly, when inner tubes are aged in the oxygen bomb, the purpose is to determine their resistance to oxidation and to disregard the influence of heat and mechanical work.

Because most rubber goods deteriorate from several influences rather than from one, and because present-day aging tests do not intensify each of the factors to the same degree, it cannot be expected that any of the aging tests duplicates exactly natural aging. Nevertheless, where the predominant effect in the artificial test is also the predominant effect in natural aging, almost the same results from a practical point of view are obtained.

Tests which intensify oxidation, heat effects, and mechanical work have been developed to a high degree of practical utility, but it still remains for some one to develop a test for simulating the effects of sunlight. The Fadeometer and ultra-violet light tests represent attempts to duplicate the effects of sunlight, but evidence thus far shows that these tests do not duplicate the effects of sunlight and only give misleading results. There is accordingly an urgent need for an aging test that will approximate the effects of sunlight.

### Limitations of Oxygen Bomb Test

As mentioned above, all aging tests thus far developed intensify one factor disproportionately, and therefore come closest to duplicating natural aging when this factor is the predominant one in natural aging. The oxygen bomb, under the conditions used in most experimental and routine work at the present time, intensifies oxidation to a very high degree. When vulcanized rubber is exposed at 60° C. to oxygen under a pressure of 300 pounds per square inch (21 kg. per sq. cm.), oxidation is so rapid, compared with after-vulcanization, for instance, that for some types of rubber mixtures, such as undercured ones or those containing a high proportion of sulfur, it may not duplicate natural aging closely enough, even when the particular mixture deteriorates chiefly from oxidation in natural aging. In cases like this it is better to carry out the oxygen bomb test under milder conditions—for example, at 50° C. and a lower pressure of oxygen. When the oxygen bomb test was first designed, there was no intention of specifying any particular range of pressure or temperature and it must be understood that this test does not in any way imply a test at 60–70° C. and a pressure of 300 pounds per square inch (21 kg. per sq. cm.) or more.

Essentially the oxygen bomb test is a method of accelerating the rate of deterioration of rubber caused by oxidation by increasing the concentration and the temperature of oxygen in the surrounding medium. Judgment must be

used in choosing the particular conditions of pressure and temperature for a particular type of rubber mixture, but whatever intensities are chosen, the test is still an "oxygen bomb test" if the pressure of oxygen exceeds that in the atmosphere. The test might better be known as a compressed oxygen test, for the bomb is only an incidental feature for safety.

The question continues to be asked—how many hours in an oxygen bomb under given conditions correspond to one year of natural aging? Assuming that oxidation is the predominant influence causing natural deterioration in the rubber mixture in question, there should be a certain number of hours in oxygen at a definite pressure and temperature which correspond to one year of natural aging in dry air in darkness at a definite and constant temperature. But the difficulty lies in the fact that in natural aging the conditions, particularly the temperature, are not constant. Most chemical reactions proceed at least twice as fast when the temperature is raised 15° F. (8.3° C.), and assuming the oxidation of rubber to be a typical chemical reaction, it is obvious that, with vulcanized rubber which deteriorates chiefly from oxidation, deterioration should be at least twice as fast at 75° F. (23.9° C.) as at 60° F. (15.6° C.). In other words, a certain number of hours in an oxygen bomb might represent one year at 75° F., but two years at 60° F. There is so much variation from place to place, and between summer and winter in each place, that the average temperature of rubber goods during a year in one place may vary far more than 15° F. (8.3° C.) from the average temperature of rubber goods elsewhere. Therefore, from a practical point of view it is impossible to designate so many hours in an oxygen bomb as the equivalent of so many years of natural aging.

Because of this impossibility it is necessary, as in so many other laboratory tests, to run control tests. In other words, instead of assuming that an oxygen bomb test of a certain number of hours represents definitely a certain period of natural aging, it is better to determine the relative aging of the sample in question with a vulcanizate of known aging properties. For example, an unknown sample is aged for 200 hours in oxygen under 150 pounds (10.6 kg. per sq. cm.) pressure at 50° C., and at the same time a control, the aging of which is known to be satisfactory for the use concerned, is also aged. The comparative aging in oxygen will then give the needed information about the unknown sample. If in the oxygen bomb the aging of unknown samples is compared with the aging of known samples, then all the practical information which is ordinarily desired is obtained without the use of a fallacious comparison of number of hours in a bomb with number of years of natural aging.

In this way the oxygen bomb test may be depended upon to give reliable information about the aging properties of

rubber products which deteriorate chiefly from oxidation. Its great utility is well illustrated by the story of the company which found discordant results between the 70° C. oven test and the oxygen bomb test in developing a new inner tube. The oven test indicated an excellent stock, while the oxygen bomb test gave warning that the tubes would deteriorate too soon. Trusting the more favorable oven test, the inner tubes were sold, and within one year tubes valued at $150,000 were returned because of bad aging. Another concern, which supplies inner tubes to certain bus companies, received the complaint that its tubes became soft and tacky after 5000 miles. By the aid of the oxygen bomb test this company was able to develop inner tubes which after 20,000 miles were still in good condition.

It is unnecessary to cite further examples to show the value of the oxygen bomb test in foreseeing the natural aging of rubber products which deteriorate chiefly from oxidation. But this test is not sufficient, for the importance which sunlight, for instance, plays in the aging of some of the most important of products demands that an artificial test be developed for this kind of aging. Until tests other than those involving oxidation in darkness are developed, the rubber industry will remain without any means of foreseeing the natural aging of some of its most important products.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1009. November, 1929.]

# Natural *vs.* Artificial Aging

**Stanley Krall**

FISK RUBBER COMPANY, CHICOPEE FALLS, MASS.

A CONSIDERABLE number of types of artificial aging are being used today in an endeavor to determine the aging properties of rubber stocks in a short period of time without waiting for natural aging results. The data reported here were taken from some that are being obtained by Sub-Committee XV, Committee D-11 of the American Society for Testing Materials.

## Experimental

Three types of pneumatic tire stocks were aged by two natural and two artificial methods:

(1) Slabs were hung separately in the dark.
(2) Slabs were hung separately exposed to the weather.
(3) One-inch (2.5-cm.) wide strips were hung separately in the Geer (*2*) oven at 158° F. (70° C.).
(4) One-inch (2.5-cm.) wide strips were hung separately in the Bierer (*1*) oxygen bomb at 158° F. (70° C.) and 300 pounds (21 kg. per sq. cm.) oxygen pressure.

The stocks tested were a pure gum stock, a first grade, and a reclaim tread stock as follows:

| | STOCK 1 | STOCK 2 | STOCK 3 |
|---|---|---|---|
| Smoked sheets | 100.00 | 100.00 | 60.0 |
| Whole tire reclaim | .... | .... | 66.0 |
| D. O. T. G. | 0.75 | 1.25 | 1.0 |
| Sulfur | 3.00 | 3.50 | 3.5 |
| Zinc oxide | 5.00 | 5.00 | 5.0 |
| Carbon black | .... | 40.00 | 35.0 |
| Mineral rubber | .... | 5.00 | 5.0 |
| Pine tar | .... | 2.00 | 2.0 |
| | 108.75 | 156.75 | 177.5 |

The stocks were cured 45 and 60 minutes at 287° F. (141.7° C.). The stocks were tested after 6 and 12 months' dark aging; 3, 6, 9, and 12 months' weather exposure; 3 and 7 days in the oven; 12 and 24 hours in the bomb.

## Results

The results were plotted on a scale of 3 days in the oven and 12 hours in the bomb, equivalent to one year's natural

aging. Charts 1 and 2 show the load at break values; 3 and 4 the load at 500 per cent for stock 1 and at 300 per cent for stocks 2 and 3; 5 and 6 the percentage elongation at break; 7 and 8 the tensile product.

Chart 9 shows the relation between the days in the oven and hours in the bomb versus months in the dark. These results were obtained from the load at break curves on Charts 1 and 2. The results indicate that one year of dark aging is equivalent to approximately:

| Stock | 45-Minute Cure | | 60-Minute Cure | |
|---|---|---|---|---|
| | Days in oven | Hours in bomb | Days in oven | Hours in bomb |
| 1 | 2 | 15 | 3 | 16 |
| 2 | 3 | 9 | 3 | 8 |
| 3 | 6 | 10 | 5 | 11 |

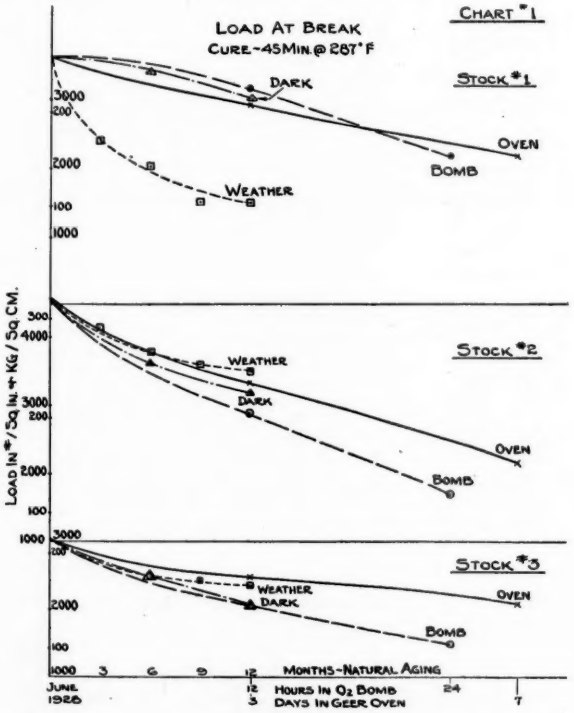
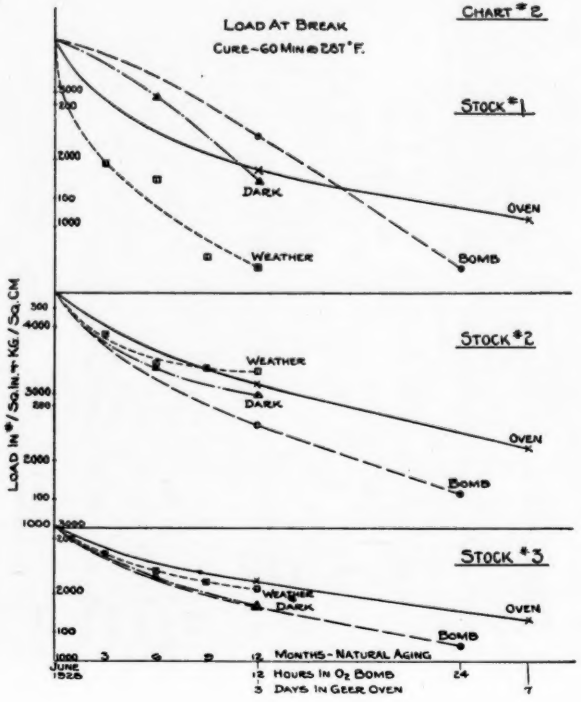
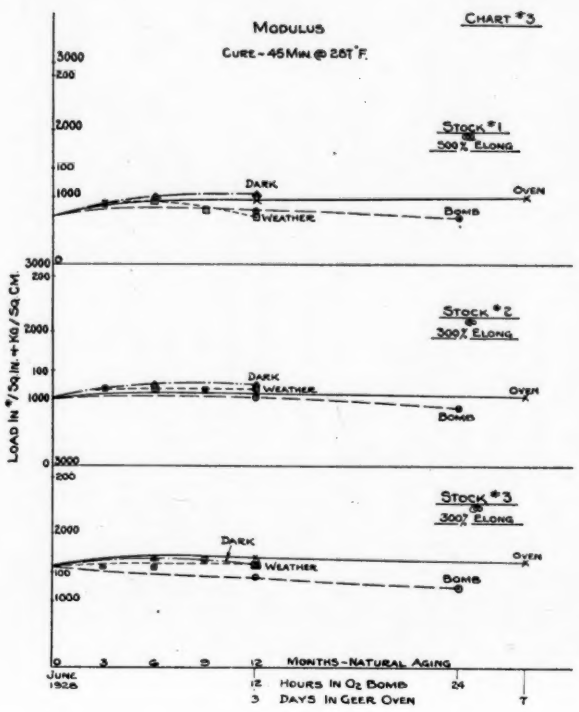



Chart 10 shows the relation between the days in the oven and hours in the bomb versus months weather exposure. The results were obtained from the load at break curves on Charts 1 and 2. These results indicate that one year of natural aging is equivalent to approximately:

| Stock | 45-Minute Cure | | 60-Minute Cure | |
|---|---|---|---|---|
| | Days in oven | Hours in bomb | Days in oven | Hours in bomb |
| 1 | ? | ? | ? | ? |
| 2 | 2–3 | 6–8 | 2–3 | 6–8 |
| 3 | 3–5 | 6–8 | 3–4 | 8–10 |

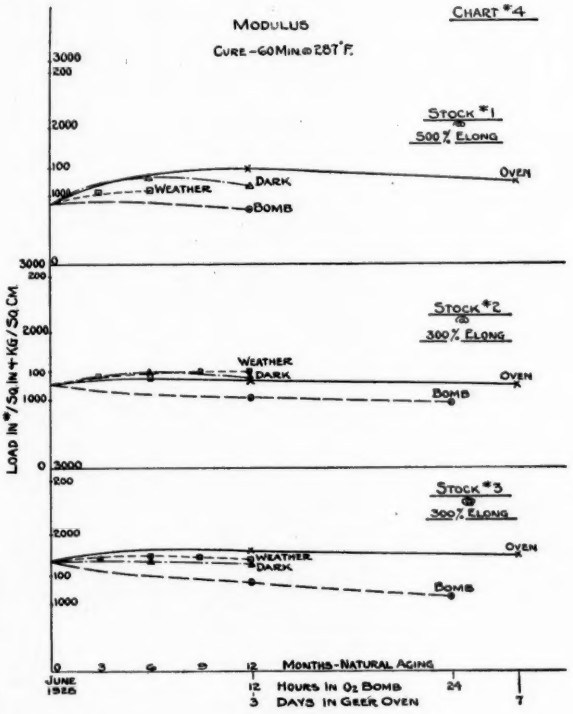

LOAD AT BREAK
CURE - 60 MIN @ 287°F.
CHART #2
STOCK #1
DARK
OVEN
WEATHER
BOMB
STOCK #2
WEATHER
DARK
OVEN
BOMB
STOCK #3
WEATHER
DARK
OVEN
BOMB
LOAD IN #/SQ.IN. = KG/SQ.CM.
3000
2000
1000
100
200
300
4000
3 6 9 12 MONTHS - NATURAL AGING
JUNE 1926
12 HOURS IN O2 BOMB
24
3 DAYS IN GEER OVEN
7


MODULUS
CURE - 45 MIN @ 287°F.
CHART #3
STOCK #1
500% ELONG
DARK
OVEN
WEATHER
BOMB
STOCK #2
300% ELONG
DARK
WEATHER
OVEN
BOMB
STOCK #3
300% ELONG
DARK
WEATHER
OVEN
BOMB
LOAD IN #/SQ.IN. = KG/SQ.CM.
3000
2000
1000
100
200
0
3 6 9 12 MONTHS - NATURAL AGING
JUNE 1926
12 HOURS IN O2 BOMB
24
3 DAYS IN GEER OVEN
7

It is difficult to draw a comparison for stock 1, probably owing to the checking (alligator-skin effect) which developed on it after a few months of weather exposure.

The curves show clearly the more rapid aging in the hot bright sunlight of the summer months as against the slower aging for the colder months (aging began June 1).

Chart 11 shows the relation between days in the oven versus hours in the bomb. The results were obtained from the load at break curves on Charts 1 and 2, and indicate that one day in the oven is equivalent to approximately:

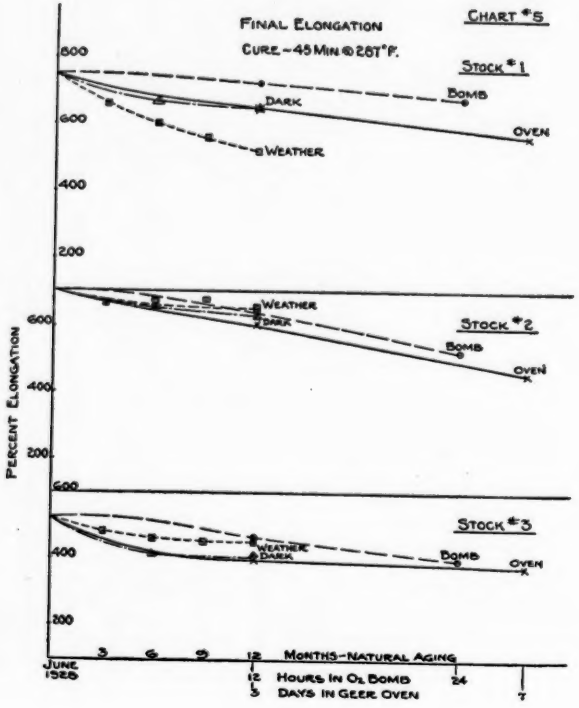


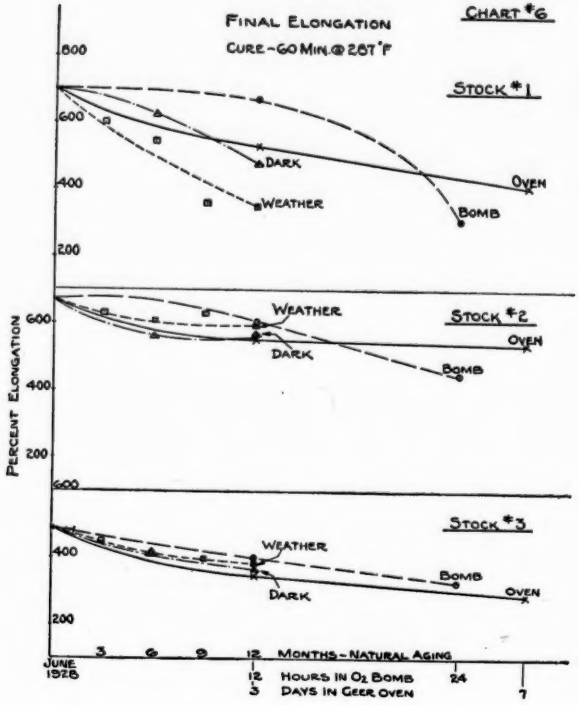

| Stock | 45-Minute Cure Hours in bomb | 60-Minute Cure Hours in bomb |
|---|---|---|
| 1 | ? | ? |
| 2 | 2½ | 2 |
| 3 | 1¾ | 2 |

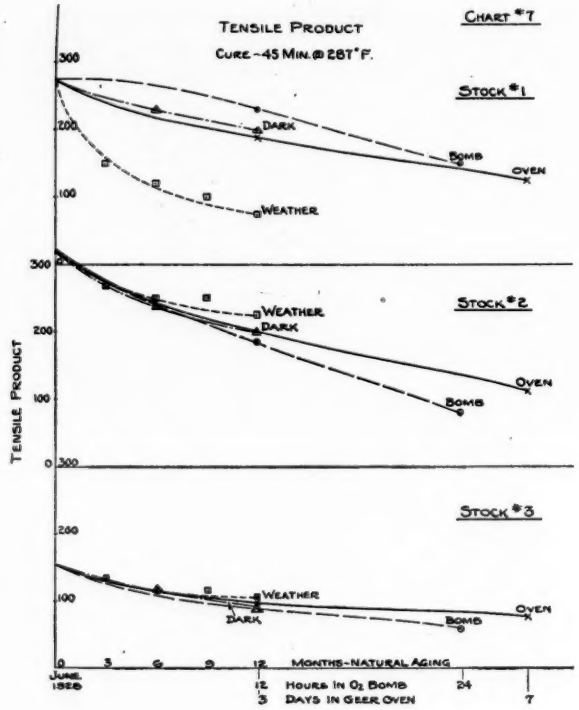
It is difficult to draw a comparison for stock 1 owing to the change in rate of aging for this stock.

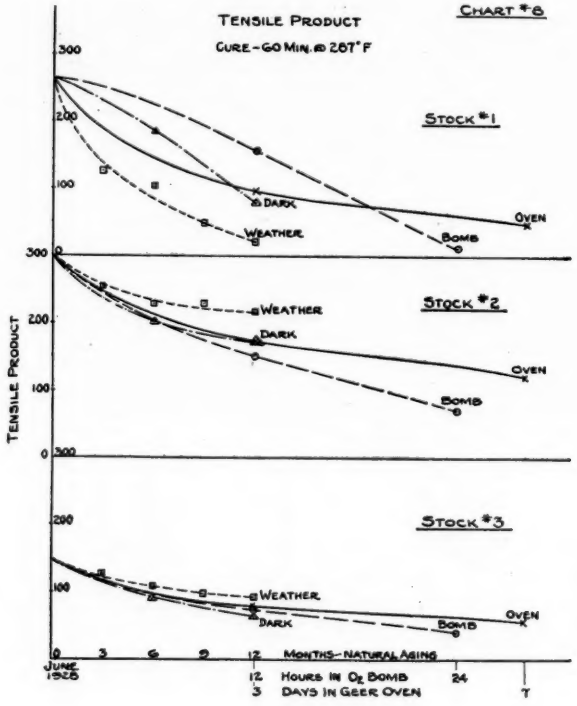
## Conclusions

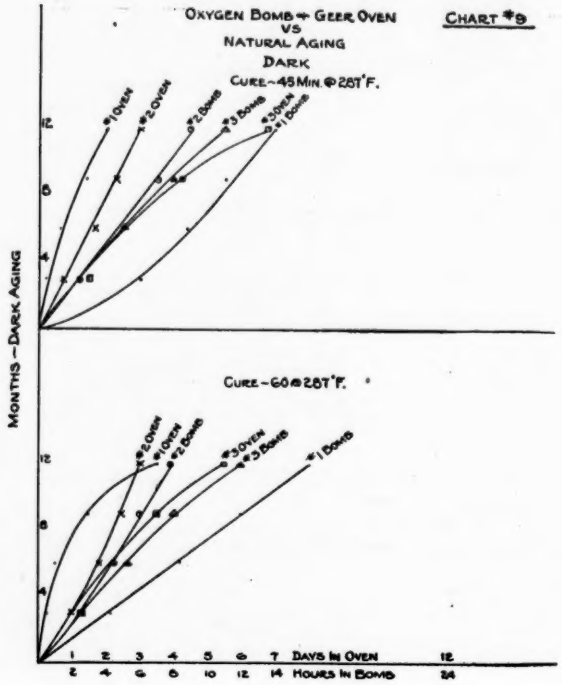
The results show that, for all stocks, there is no general correlation between either method of artificial aging and either method of natural aging. Therefore a general state-

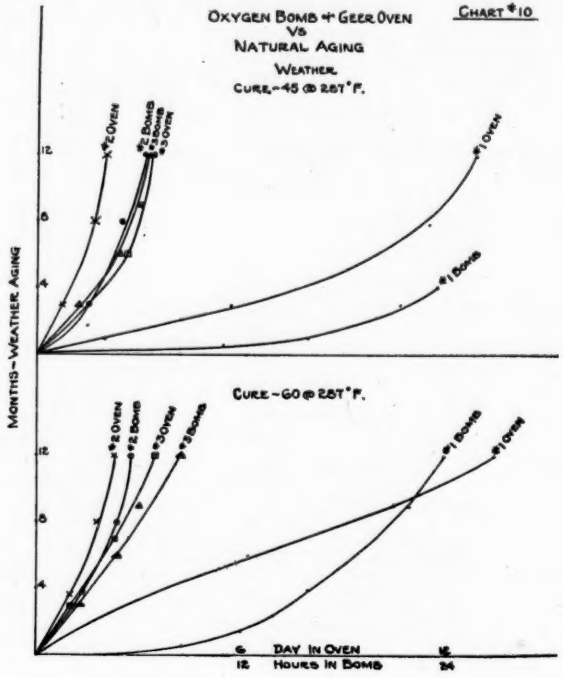

FINAL ELONGATION
CHART #5
CURE - 45 MIN @ 287°F.
STOCK #1
BOMB
DARK
OVEN
WEATHER
STOCK #2
WEATHER
DARK
BOMB
OVEN
STOCK #3
WEATHER
DARK
BOMB
OVEN
PERCENT ELONGATION
600
400
200
3 6 9 12 MONTHS - NATURAL AGING
JUNE 1928
12 HOURS IN O2 BOMB
3 DAYS IN GEER OVEN
24
7


FINAL ELONGATION
CHART #6
CURE - 60 MIN. @ 287°F
STOCK #1
DARK
OVEN
WEATHER
BOMB
STOCK #2
WEATHER
OVEN
DARK
BOMB
STOCK #3
WEATHER
BOMB
DARK
OVEN
PERCENT ELONGATION
600
400
200
3 6 9 12 MONTHS - NATURAL AGING
JUNE 1928
12 HOURS IN O2 BOMB
3 DAYS IN GEER OVEN
24
7

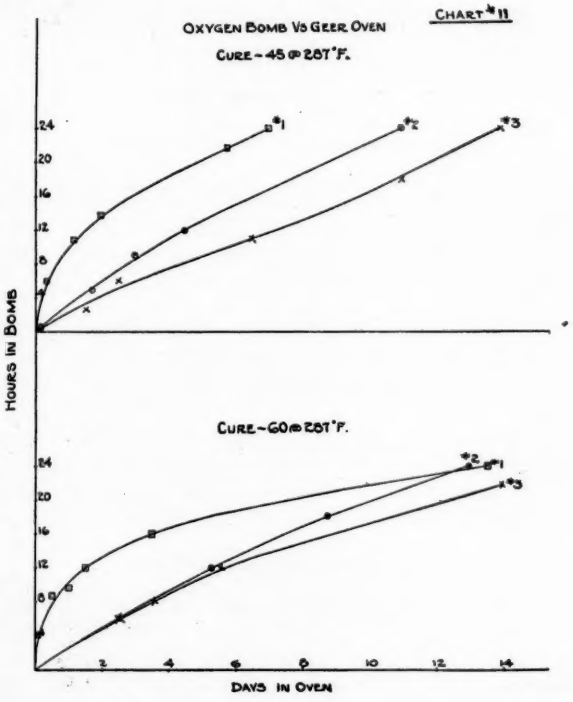

TENSILE PRODUCT
CURE - 45 MIN. @ 287°F.
CHART #7
STOCK #1
DARK
BOMB
OVEN
WEATHER
STOCK #2
WEATHER
DARK
OVEN
BOMB
STOCK #3
WEATHER
OVEN
DARK
BOMB
TENSILE PRODUCT
300
200
100
0
0 3 6 9 12 MONTHS - NATURAL AGING
JUNE 1926
12 HOURS IN O2 BOMB
3 DAYS IN GEER OVEN
24
7


TENSILE PRODUCT
CURE - 60 MIN. @ 287°F
CHART #8
STOCK #1
DARK
WEATHER
BOMB
OVEN
STOCK #2
WEATHER
DARK
OVEN
BOMB
STOCK #3
WEATHER
OVEN
DARK
BOMB
TENSILE PRODUCT
300
200
100
0
0 3 6 9 12 MONTHS - NATURAL AGING
JUNE 1926
12 HOURS IN O2 BOMB
3 DAYS IN GEER OVEN
24
7


OXYGEN BOMB & GEER OVEN
VS
NATURAL AGING
DARK
CURE-45 MIN. @ 281°F.
CHART #9
#1 OVEN
#2 OVEN
#2 BOMB
#3 BOMB
#3 OVEN
#1 BOMB
CURE-60 @ 281°F.
#2 OVEN
#1 OVEN
#2 BOMB
#3 OVEN
#3 BOMB
#1 BOMB
MONTHS - DARK AGING
4
8
12
1 2 3 4 5 6 7 DAYS IN OVEN 12
2 4 6 8 10 12 14 HOURS IN BOMB 24


OXYGEN BOMB & GEER OVEN
VS
NATURAL AGING
WEATHER
CURE-45 @ 281°F.
CHART #10
#2 OVEN
#2 BOMB
#3 BOMB
#3 OVEN
#1 OVEN
#1 BOMB
CURE-60 @ 281°F.
#2 OVEN
#2 BOMB
#3 OVEN
#3 BOMB
#1 BOMB
#1 OVEN
MONTHS - WEATHER AGING
4
8
12
6 DAY IN OVEN 15
12 HOURS IN BOMB 24

ment cannot be made in regard to a time in the bomb or oven which will duplicate a definite period of natural aging. However, the trend of the natural aging–physical property curves can be duplicated by either artificial method, but the rate of artificial aging by either method must be determined for each particular stock. There is such a wide variation in the type of natural aging to which rubber products are subjected, such as heat, oxidation, light, etc., as well as a combination of any of them, that it is very important that the method of artificial aging be one that will best duplicate the aging and service conditions to which any particular stock is subjected.




## Acknowledgment

Acknowledgment is due B. N. Larsen for his valuable assistance in preparing this paper.

## Literature Cited

(1) Bierer, IND. ENG. CHEM., **16**, 711 (1924).
(2) Geer, *India Rubber World*, **64**, 887 (1921).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1012. November, 1929.]

# Accelerated Aging *vs.* Shelf Aging

**Everett M. Follansbee**

SIMPLEX WIRE & CABLE CO., BOSTON, MASS.

SAMPLES of rubber-insulated wire were aged by exposing to the diffused light in the physical testing laboratory. The thickness of wall of rubber surrounding the tinned copper wire showed a variation from 0.030 to 0.065 inch (0.76 to 1.65 mm.).

The samples were tested for tensile strength and elongation during the aging interval and the results were then compared with accelerated life tests obtained on the same samples when new.

Average results on 480 different compounds, ranging in quality from a low-grade compound to a compound containing 60 per cent by weight of crude rubber, show the following relationship between shelf aging and accelerated aging.

**Equivalent Years of Shelf Aging**

| | HEATED 96 HOURS AT 70° C. IN AIR | HEATED 24 HOURS IN OXYGEN AT 60° C. AND 300 LBS. (21.1 KG.) PRESSURE |
|---|---|---|
| | *Years* | *Years* |
| Tensile strength | 1.43 | 1.37 |
| Elongation | 1.18 | 1.00 |

Both of these accelerated aging tests give a longer shelf-aging time equivalent for tensile strength than is given for elongation.

The Geer test (96 hours at 70° C. in air) on the average represents the same shelf-aging time regardless of the type of compound. The oxygen test, however, in the case of elongation, represents a much shorter shelf-aging time for the lower grade compounds.

Both of the accelerated aging tests gave results that varied considerably in equivalent time for shelf aging, and it should be emphasized that the above equivalent aging results are only average figures.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1013, November, 1929.]

# Aging of Mechanical Rubber Goods Stocks by Various Methods

**K. J. Soule**

MANHATTAN RUBBER MFG. CO., PASSAIC, N. J.

THIS paper records the aging of thirty typical mechanical rubber goods stocks, all of which are, or have been, in regular factory use over long periods of time. The times of aging used are 1 year of natural aging in the dark; 24 hours and 48 hours in the oxygen bomb at 60° C. and 300 pounds (21 kg. per sq. cm.) pressure; and 96 hours at 70° C. in the Geer oven. These stocks are arranged in three groups: (1) lightly compounded, three stocks; (2) medium compounded, twenty stocks; and (3) heavily compounded, seven stocks.

The physical properties studied are tensile strength, elongation, tensile product, and modulus. The percentage increase or decrease in each of these properties after each type of aging is recorded. (Tables I to III)

Figures 1 to 6, inclusive, show graphically the changes in the physical properties studied on each of the three lightly compounded stocks, using several different methods of presenting the data.

Table IV shows the coefficient of correlation and the probable error of this coefficient for oven and bomb aging on each of the three types of stock. For the correlation to be at all marked, the value should be in excess of 0.5, the value ±1.0 representing perfect correlation. As a further check, the value for each coefficient of correlation should be greater than four times its probable error.

Figure 7 illustrates graphically the data presented in Table IV. It will be noted that neither bomb nor oven aging shows satisfactory correlation with natural aging for all types of stocks examined, or for all of the physical properties of any one class of stock. In fact, as far as the results obtained on the thirty compounds examined are concerned, there is practically no choice between the bomb and the oven as an approximation to natural aging.

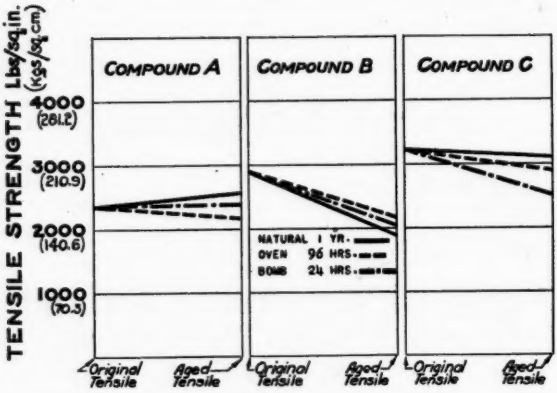



Figure 1

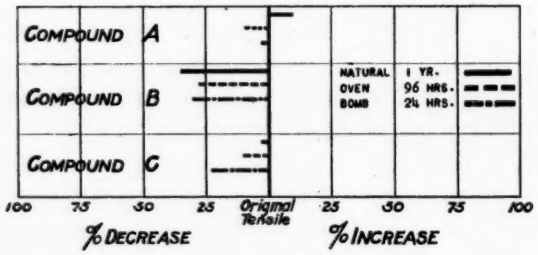



Figure 2

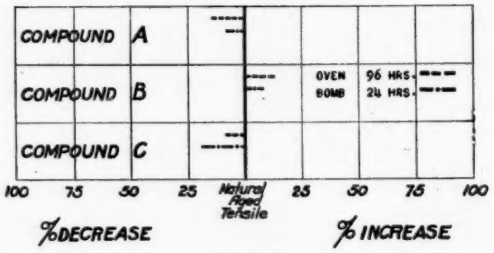



Figure 3

**Tensile Strength of Lightly Compounded Stocks**

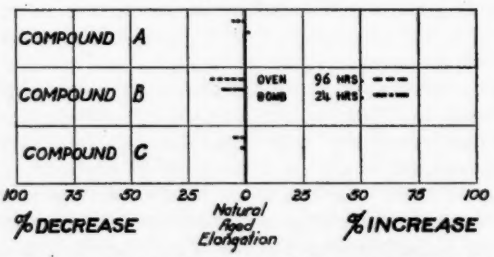



**Figure 4—Elongation of Lightly Compounded Stocks**

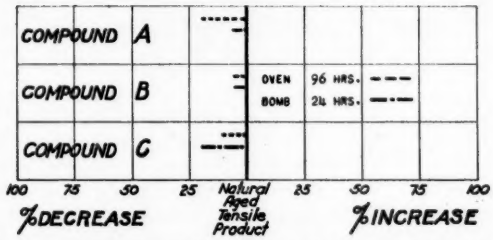



**Figure 5—Tensile Product of Lightly Compounded Stocks**

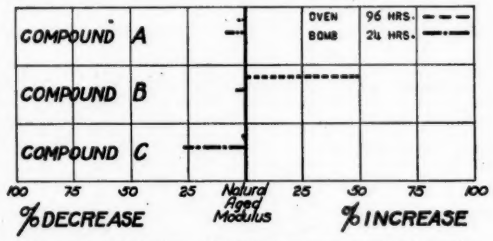



**Figure 6—Modulus of Lightly Compounded Stocks**

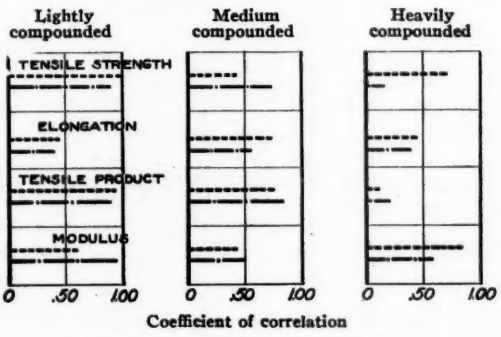



**Figure 7—Coefficients of Correlation**

**Table I—Aging Data for Lightly Compounded Stocks**

| | Aging | Modulus | | Tensile | | Elongation | | Tensile Product | |
|---|---|---|---|---|---|---|---|---|---|
| | | *Kg./sq. cm.* | *% change* | *Kg./sq. cm.* | *% change* | *%* | *% change* | *%* | *% change* |
| | | (600%) | | | | | | | |
| (1) | Original | 133 | | 165 | | 650 | | 153 | |
| | Natural aging, 1 year | 158 | +18 | 180 | + 9 | 625 | − 4 | 160 | + 5 |
| | Oven, 96 hours, 70° C. | 151 | +13 | 152 | − 8 | 600 | − 8 | 130 | −15 |
| | Bomb, 24 hours, 60° C. | 144 | + 8 | 168 | + 1 | 630 | − 3 | 150 | − 2 |
| | Bomb, 48 hours, 60° C. | 144 | + 8 | 175 | + 6 | 640 | − 2 | 159 | + 4 |
| | | (500%) | | | | | | | |
| (2) | Original | 147 | | 204 | | 600 | | 175 | |
| | Natural aging, 1 year | 98 | −33 | 135 | −34 | 600 | 00 | 116 | −34 |
| | Oven, 96 hours, 70° C. | 147 | 00 | 151 | −26 | 512 | −15 | 111 | −37 |
| | Bomb, 24 hours, 60° C. | 95 | −36 | 146 | −29 | 537 | −10 | 112 | −36 |
| | Bomb, 48 hours, 60° C. | 72 | −51 | 110 | −46 | 562 | − 6 | 88 | −50 |
| | | (600%) | | | | | | | |
| (3) | Original | 112 | | 223 | | 725 | | 231 | |
| | Natural aging, 1 year | 95 | −16 | 219 | − 2 | 750 | + 3 | 234 | + 1 |
| | Oven, 96 hours, 70° C. | 95 | −16 | 204 | − 8 | 720 | − 1 | 210 | − 9 |
| | Bomb, 24 hours, 60° C. | 70 | −37 | 174 | −22 | 745 | + 3 | 185 | −20 |
| | Bomb, 48 hours, 60° C. | 77 | −31 | 138 | −38 | 700 | − 3 | 138 | −40 |

**Table II—Aging Data for Medium Compounded Stocks**

| Aging | Modulus | | Tensile | | Elongation | | Tensile Product | |
|---|---|---|---|---|---|---|---|---|
| | *Kg./sq. cm.* | *% change* | *Kg./sq. cm.* | *% change* | *%* | *% change* | | *% change* |
| | (500%) | | | | | | | |
| (1) Original | 98 | | 173 | | 642 | | 158 | |
| Natural aging, 1 year | 102 | + 4 | 130 | −25 | 562 | −12 | 105 | −34 |
| Oven, 96 hours, 70° C. | 138 | +41 | 138 | −20 | 500 | −22 | 99 | −37 |
| Bomb, 24 hours, 60° C. | 116 | +18 | 136 | −21 | 525 | −18 | 102 | −35 |
| Bomb, 48 hours, 60° C. | ... | .. | 96 | −45 | 475 | −26 | 65 | −59 |
| | (500%) | | | | | | | |
| (2) Original | 123 | | 248 | | 657 | | 232 | |
| Natural aging, 1 year | 121 | − 1 | 198 | −20 | 620 | − 6 | 176 | −24 |
| Oven, 96 hours, 70° C. | 109 | −11 | 184 | −26 | 603 | − 8 | 158 | −32 |
| Bomb, 24 hours, 60° C. | ... | .. | ... | .. | ... | .. | ... | .. |
| Bomb, 48 hours, 60° C. | ... | .. | ... | .. | ... | .. | ... | .. |
| | (300%) | | | | | | | |
| (3) Original | 46 | | 79 | | 437 | | 49 | |
| Natural aging, 1 year | 50 | + 9 | 58 | −26 | 369 | −16 | 31 | −37 |
| Oven, 96 hours, 70° C. | 57 | +25 | 68 | −14 | 360 | −18 | 35 | −29 |
| Bomb, 24 hours, 60° C. | 40 | −11 | 55 | −31 | 405 | − 7 | 32 | −35 |
| Bomb, 48 hours, 60° C. | 38 | −15 | 44 | −44 | 360 | −17 | 23 | −53 |
| | (300%) | | | | | | | |
| (4) Original | 51 | | 67 | | 400 | | 38 | |
| Natural aging, 1 year | 49 | − 4 | 53 | −21 | 350 | −12 | 27 | −29 |
| Oven, 96 hours, 70° C. | 67 | +30 | 66 | − 2 | 300 | −25 | 28 | −26 |
| Bomb, 24 hours, 60° C. | 46 | −11 | 45 | −33 | 300 | −25 | 19 | −50 |
| Bomb, 48 hours, 60° C. | ... | .. | 36 | −47 | 200 | −50 | 10 | −73 |
| | (300%) | | | | | | | |
| (5) Original | 77 | | 114 | | 400 | | 65 | |
| Natural aging, 1 year | 95 | +23 | 105 | − 7 | 342 | −14 | 51 | −21 |
| Oven, 96 hours, 70° C. | 86 | +11 | 100 | −12 | 350 | −12 | 50 | −23 |
| Bomb, 24 hours, 60° C. | 70 | − 9 | 84 | −26 | 370 | − 7 | 44 | −32 |
| Bomb, 48 hours, 60° C. | 71 | − 8 | 71 | −38 | 300 | −25 | 30 | −54 |
| | (400%) | | | | | | | |
| (6) Original | 47 | | 91 | | 537 | | 70 | |
| Natural aging, 1 year | 42 | −11 | 68 | −25 | 525 | − 2 | 51 | −27 |
| Oven, 96 hours, 70° C. | 61 | +30 | 75 | −17 | 440 | −18 | 47 | −33 |
| Bomb, 24 hours, 60° C. | 47 | −00 | 65 | −29 | 487 | − 9 | 45 | −36 |
| Bomb, 48 hours, 60° C. | 45 | − 4 | 54 | −40 | 440 | −18 | 34 | −51 |
| | (300%) | | | | | | | |
| (7) Original | 67 | | 111 | | 450 | | 71 | |
| Natural aging, 1 year | 84 | +26 | 89 | −20 | 324 | −28 | 41 | −42 |
| Oven, 96 hours, 70° C. | 98 | +47 | 100 | −10 | 310 | −31 | 44 | −38 |
| Bomb, 24 hours, 60° C. | 55 | −17 | 84 | −24 | 410 | − 9 | 49 | −31 |
| Bomb, 48 hours, 60° C. | 65 | − 3 | 84 | −24 | 387 | −14 | 46 | −35 |
| | (500%) | | | | | | | |
| (8) Original | 137 | | 170 | | 555 | | 134 | |
| Natural aging, 1 year | 137 | 00 | 155 | − 9 | 543 | − 2 | 120 | −10 |
| Oven, 96 hours, 70° C. | 103 | −24 | 124 | −27 | 550 | − 1 | 97 | −28 |
| Bomb, 24 hours, 60° C. | 119 | −13 | 145 | −15 | 550 | − 1 | 113 | −16 |
| Bomb, 48 hours, 60° C. | 109 | −20 | 129 | −24 | 550 | − 1 | 101 | −25 |
| | (400%) | | | | | | | |
| (9) Original | 46 | | 80 | | 575 | | 66 | |
| Natural aging, 1 year | 46 | 0 | 55 | −31 | 450 | −22 | 35 | −47 |
| Oven, 96 hours, 70° C. | 44 | − 4 | 49 | −39 | 445 | −23 | 31 | −53 |
| Bomb, 24 hours, 60° C. | 35 | −23 | 55 | −31 | 525 | − 9 | 41 | −38 |
| Bomb, 48 hours, 60° C. | 30 | −35 | 48 | −41 | 515 | −10 | 35 | −47 |
| | (300%) | | | | | | | |
| (10) Original | 60 | | 133 | | 520 | | 99 | |
| Natural aging, 1 year | 75 | +26 | 105 | −21 | 418 | −19 | 63 | −36 |
| Oven, 96 hours, 70° C. | 77 | +29 | 94 | −29 | 355 | −32 | 48 | −51 |
| Bomb, 24 hours, 60° C. | 58 | − 3 | 95 | −28 | 450 | −13 | 61 | −38 |
| Bomb, 48 hours, 60° C. | 56 | − 6 | 86 | −35 | 325 | −37 | 40 | −60 |

**Table II** (*Continued*)

| | Aging | Modulus Kg./sq. cm. | % change | Tensile Kg./sq. cm. | % change | Elongation % | % change | Tensile Product | % change |
|---|---|---|---|---|---|---|---|---|---|
| | (600%) | | | | | | | | |
| (11) | Original | 154 | | 256 | | 750 | | 274 | |
| | Natural aging, 1 year | 182 | +18 | 266 | + 4 | 725 | − 3 | 274 | 00 |
| | Oven, 96 hours, 70° C. | 168 | + 9 | 260 | + 2 | 706 | − 6 | 262 | − 4 |
| | Bomb, 24 hours, 60° C. | 162 | + 5 | 244 | − 5 | 725 | − 3 | 252 | − 8 |
| | Bomb, 48 hours, 60° C. | 163 | + 6 | 234 | − 8 | 700 | − 7 | 234 | −14 |
| | (300%) | | | | | | | | |
| (12) | Original | 75 | | 99 | | 430 | | 61 | |
| | Natural aging, 1 year | 67 | −12 | 70 | −29 | 325 | −24 | 32 | −48 |
| | Oven, 96 hours, 70° C. | 92 | +23 | 95 | − 4 | 312 | −27 | 42 | −31 |
| | Bomb, 24 hours, 60° C. | 61 | −19 | 60 | −39 | 287 | −33 | 25 | −59 |
| | Bomb, 48 hours, 60° C. | ... | .. | 52 | −48 | 200 | −53 | 15 | −75 |
| | (500%) | | | | | | | | |
| (13) | Original | 140 | | 210 | | 605 | | 181 | |
| | Natural aging, 1 year | 119 | −15 | 190 | − 9 | 643 | + 6 | 174 | − 4 |
| | Oven, 96 hours, 70° C. | 154 | +10 | 190 | −10 | 562 | − 7 | 152 | −16 |
| | Bomb, 24 hours, 60° C. | 112 | −20 | 174 | −17 | 625 | + 3 | 155 | −14 |
| | Bomb, 48 hours, 70° C. | 126 | −10 | 179 | −15 | 600 | − 1 | 153 | −15 |
| | (500%) | | | | | | | | |
| (14) | Original | 87 | | 193 | | 650 | | 179 | |
| | Natural aging, 1 year | 101 | +15 | 141 | −27 | 575 | −12 | 116 | −35 |
| | Oven, 96 hours, 70° C. | 107 | +22 | 154 | −20 | 600 | − 8 | 131 | −27 |
| | Bomb, 24 hours, 60° C. | 97 | +11 | 142 | −26 | 600 | − 8 | 121 | −32 |
| | Bomb, 48 hours, 60° C. | 94 | + 7 | 119 | −38 | 550 | −15 | 93 | −48 |
| | (500%) | | | | | | | | |
| (15) | Original | 87 | | 190 | | 675 | | 182 | |
| | Natural aging, 1 year | 94 | + 6 | 134 | −29 | 587 | −13 | 112 | −38 |
| | Oven, 96 hours, 70° C. | 77 | −14 | 141 | −26 | 640 | − 5 | 129 | −29 |
| | Bomb, 24 hours, 60° C. | 80 | −10 | 140 | −26 | 625 | − 7 | 125 | −31 |
| | Bomb, 48 hours, 60° C. | 67 | −25 | 124 | −35 | 627 | − 7 | 111 | −39 |
| | (300%) | | | | | | | | |
| (16) | Original | 63 | | 85 | | 400 | | 50 | |
| | Natural aging, 1 year | 55 | −12 | 64 | −26 | 350 | −12 | 32 | −36 |
| | Oven, 96 hours, 70° C. | 70 | +11 | 71 | −12 | 337 | −16 | 37 | −26 |
| | Bomb, 24 hours, 60° C. | 65 | + 3 | 77 | −11 | 350 | −12 | 39 | −22 |
| | Bomb, 48 hours, 60° C. | 61 | − 3 | 67 | −23 | 350 | −12 | 33 | −34 |
| | (500%) | | | | | | | | |
| (17) | Original | 64 | | 156 | | 690 | | 153 | |
| | Natural aging, 1 year | 73 | +15 | 152 | − 3 | 675 | − 2 | 146 | − 5 |
| | Oven, 96 hours, 70° C. | 65 | + 2 | 123 | −21 | 650 | − 6 | 113 | −26 |
| | Bomb, 24 hours, 60° C. | 56 | −12 | 135 | −13 | 675 | − 2 | 130 | −15 |
| | Bomb, 48 hours, 60° C. | 51 | −20 | 85 | −46 | 625 | − 9 | 76 | −50 |
| | (400%) | | | | | | | | |
| (18) | Original | 34 | | 55 | | 530 | | 41 | |
| | Natural aging, 1 year | 46 | +33 | 52 | − 5 | 437 | −18 | 32 | −22 |
| | Oven, 96 hours, 70° C. | 46 | +33 | 48 | −12 | 425 | −20 | 29 | −29 |
| | Bomb, 24 hours, 60° C. | 36 | + 4 | 50 | − 9 | 490 | − 8 | 35 | −15 |
| | Bomb, 48 hours, 60° C. | 35 | + 2 | 46 | −16 | 470 | −11 | 31 | −24 |
| | (500%) | | | | | | | | |
| (19) | Original | 65 | | 92 | | 630 | | 83 | |
| | Natural aging, 1 year | 72 | +13 | 92 | − 1 | 575 | − 9 | 76 | − 8 |
| | Oven, 96 hours, 70° C. | 71 | +10 | 90 | − 2 | 562 | −11 | 72 | −13 |
| | Bomb, 24 hours, 60° C. | 62 | − 3 | 88 | − 4 | 600 | − 5 | 76 | − 8 |
| | Bomb, 48 hours, 60° C. | 56 | −13 | 68 | −26 | 555 | −12 | 54 | −35 |
| | (300%) | | | | | | | | |
| (20) | Original | 43 | | 95 | | 430 | | 58 | |
| | Natural aging, 1 year | 67 | +55 | 85 | −10 | 375 | −13 | 46 | −21 |
| | Oven, 96 hours, 70° C. | 63 | +46 | 84 | −12 | 375 | −13 | 45 | −22 |
| | Bomb, 24 hours, 60° C. | 55 | +27 | 84 | −12 | 410 | − 5 | 49 | −16 |
| | Bomb, 48 hours, 60° C. | 55 | +26 | 76 | −19 | 395 | − 8 | 43 | −26 |

**Table III—Aging Data for Heavily Compounded Stocks**

| Aging | Modulus | | Tensile | | Elongation | | Tensile Product | |
|---|---|---|---|---|---|---|---|---|
| | Kg./sq. cm. | % change | Kg./sq. cm. | % change | % | % change | | % change |
| | (500%) | | | | | | | |
| (1) Original | 54 | | 84 | | 600 | | 72 | |
| Natural aging, 1 year | 68 | +26 | 70 | −16 | 506 | −16 | 51 | −29 |
| Oven, 96 hours, 70° C. | 47 | −13 | 66 | −22 | 587 | − 2 | 55 | −24 |
| Bomb, 24 hours, 60° C. | 47 | −13 | 76 | − 9 | 610 | + 2 | 66 | − 8 |
| Bomb, 48 hours, 60° C. | 44 | −19 | 70 | −16 | 600 | 0 | 60 | −17 |
| | (400%) | | | | | | | |
| (2) Original | 46 | | 62 | | 500 | | 44 | |
| Natural aging, 1 year | 33 | −28 | 34 | −45 | 406 | −19 | 20 | −54 |
| Oven, 96 hours, 70° C. | 71 | +53 | 72 | +16 | 400 | −20 | 41 | − 7 |
| Bomb, 24 hours, 60° C. | 64 | +38 | 64 | + 3 | 400 | −20 | 36 | −18 |
| Bomb, 48 hours, 60° C. | 54 | +17 | 54 | −12 | 400 | −20 | 31 | −30 |
| | (500%) | | | | | | | |
| (3) Original | 147 | | 190 | | 562 | | 152 | |
| Natural aging, 1 year | 147 | 0 | 183 | − 4 | 575 | + 2 | 150 | − 1 |
| Oven, 96 hours, 70° C. | 156 | + 6 | 169 | −11 | 520 | − 7 | 125 | −18 |
| Bomb, 24 hours, 60° C. | 133 | −10 | 149 | −22 | 535 | − 4 | 113 | −26 |
| Bomb, 48 hours, 60° C. | 139 | − 6 | 158 | −17 | 540 | − 4 | 122 | −20 |
| | (300%) | | | | | | | |
| (4) Original | 41 | | 65 | | 410 | | 38 | |
| Natural aging, 1 year | 46 | +10 | 43 | −34 | 295 | −28 | 18 | −53 |
| Oven, 96 hours, 70° C. | 47 | +14 | 57 | −12 | 362 | −12 | 29 | −24 |
| Bomb, 24 hours, 60° C. | 36 | −12 | 45 | −30 | 375 | − 9 | 24 | −37 |
| Bomb, 48 hours, 60° C. | 35 | −15 | 45 | −30 | 390 | − 5 | 25 | −34 |
| | (500%) | | | | | | | |
| (5) Original | 72 | | 95 | | 570 | | 78 | |
| Natural aging, 1 year | 67 | − 8 | 83 | −13 | 556 | − 2 | 66 | −15 |
| Oven, 96 hours, 70° C. | 75 | + 4 | 95 | − 1 | 565 | − 1 | 76 | − 3 |
| Bomb, 24 hours, 60° C. | 51 | −30 | 63 | −34 | 550 | − 4 | 49 | −37 |
| Bomb, 48 hours, 60° C. | 42 | −42 | 43 | −55 | 507 | −11 | 31 | −60 |
| | (300%) | | | | | | | |
| (6) Original | 63 | | 105 | | 425 | | 63 | |
| Natural aging, 1 year | 71 | +14 | 94 | −10 | 375 | −12 | 50 | −21 |
| Oven, 96 hours, 70° C. | 71 | +13 | 90 | −13 | 350 | −18 | 45 | −29 |
| Bomb, 24 hours, 60° C. | 64 | + 1 | 104 | − 1 | 440 | + 4 | 65 | + 3 |
| Bomb, 48 hours, 60° C. | 58 | − 8 | 80 | −23 | 400 | − 6 | 46 | −27 |
| | (300%) | | | | | | | |
| (7) Original | 86 | | 150 | | 440 | | 94 | |
| Natural aging, 1 year | 87 | + 2 | 136 | − 9 | 425 | − 3 | 82 | −13 |
| Oven, 96 hours, 70° C. | 90 | + 5 | 127 | −15 | 400 | − 9 | 72 | −23 |
| Bomb, 24 hours, 60° C. | 89 | + 3 | 150 | 0 | 437 | − 1 | 93 | − 1 |
| Bomb, 48 hours, 60° C. | 86 | 0 | 142 | − 5 | 443 | + 1 | 90 | − 4 |

**Table IV—Coefficients of Correlation between Oven Aging and Bomb Aging**

| Property | Oven Aging—96 Hours: Coef. of Correlation | Oven Aging—96 Hours: Probable Error | Bomb Aging—24 Hours: Coef. of Correlation | Bomb Aging—24 Hours: Probable Error | Best Approximation to Natural Aging |
|---|---|---|---|---|---|
| | Lightly Compounded Stocks | | | | |
| Modulus | 0.610 | ±0.24000 | 0.940 | ±0.04600 | Bomb |
| Tensile | 0.990 | ±0.00074 | 0.900 | ±0 07400 | Oven |
| Elongation | 0.470 | ±0.34000 | 0 390 | ±0 33000 | ... |
| Tensile product | 0.950 | ±0.03500 | 0.890 | ±0.07700 | Oven |
| | Medium Compounded Stocks | | | | |
| Modulus | 0.410 | ±0.12500 | 0.500 | ±0.11600 | ... |
| Tensile | 0.420 | ±0.18400 | 0.770 | ±0 09200 | Bomb |
| Elongation | 0.760 | ±0.06300 | 0.550 | ±0 10800 | Oven |
| Tensile product | 0.740 | ±0.06100 | 0.845 | ±0.03800 | Bomb |
| | Heavily Compounded Stocks | | | | |
| Modulus | −0.830 | ±0.07900 | −0.570 | ±0.17300 | Oven |
| Tensile | −0.720 | ±0.12200 | −0.147 | ±0 25000 | Oven |
| Elongation | 0 440 | ±0.22000 | 0 380 | ±0 22000 | ... |
| Tensile product | 0.072 | ±0.25000 | 0.200 | ±0.25000 | ... |

## Acknowledgment

Grateful acknowledgment is made of the assistance of H. A. Braendle, of Binney & Smith, for outlining the method

of working out the coefficient of correlation, and to J. M. Ball, of R. T. Vanderbilt Company, for help in drawing up the graphs.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1015. November, 1929.]

# Some Notes on Artificial Aging Tests for Rubber

W. W. Vogt

GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

FROM a strictly quantitative point of view we should expect an artificial age test to duplicate in all respects the changes that take place on natural aging. In other words, all of the measurable physical and chemical properties should be changed in the same direction and to the same degree for all types of compounds.

If we are looking for such performance from an artificial aging test, then in the writer's opinion none of the present tests fulfil these conditions to a sufficient degree to warrant any extensive use of correlation factors. It must, moreover, be realized that the present methods of artificial aging seek only to duplicate the natural aging of rubber on shelf storage in the dark. If we wish information that will predict aging of rubber products under their normal service conditions, then we must get into the field of specialized testing wherein the conditions with respect to light, temperature, humidity, etc., may be made to approach more nearly those of the actual service.

## Limitations of Present Aging Methods

With these points in mind we may now consider a few of the more serious limitations of present methods.

LIMITATION 1—All of the measurable properties should change in the same direction and to the same degree as in natural aging. In this connection the writer wishes to present a few data by C. R. Park.

The formula is—rubber 100, ZnO 12.5, PbO 6.25, and sulfur 6.25. This stock was used for several years as a tube stock. General experience and records over a long period have shown that it stiffens on aging and that the tensile qualities hold up fairly well.

From the data given in Table I we find: (1) On natural aging the tensile product decreases and the stiffness index increases. (2) In the Geer oven the tensile product decreases

and the stiffness index decreases very strongly. (3) In the Bierer-Davis bomb the tensile product increases slightly, but the stiffness index decreases quite markedly.

**Table I**

| Aging | Tensile Product[a] | Stiffness Index[b] |
|---|---|---|
| Original | 150 | 85 |
| 3 days Geer oven at 70° C. | 76 | 76 |
| 6 days Geer oven at 70° C. | 65 | 70 |
| 9 days Geer oven at 70° C. | 60 | 64 |
| 16 hours Bierer-Davis bomb (at 50° C. and 400 lbs. per sq. in. or 28.2 kg. per sq. cm.) oxygen pressure | 155 | 77 |
| 6 months natural | 140 | 95 |
| 12 months natural | 120 | 102 |

[a] Tensile in kg. per sq. cm. × elongation ÷ 1000.
[b] Difference in kg. per sq. cm. of the moduli at 650 and 450 per cent.

This behavior is typical of several similar types of litharge stocks and one is forced to conclude that it is rather hopeless to attempt their evaluation by present methods of accelerated aging.

Limitation 2—Another question that is constantly being asked is—how many hours in the oven or the bomb does it take to equal a given period of natural aging? In other words, what is the equivalence factor?

Park (*1*) and Vogt (*2*) have shown that to produce changes equivalent to those produced by a given period of natural aging the times required for both the oven and the bomb test vary as much as tenfold depending upon the type of stock. This extreme variation can only force us to the conclusion that in the present state of the art accelerated aging cannot be said to be a quantitative method.

Even under the most ideal conditions one can get very diversified results as to the equivalence factor, depending upon what property one chooses upon which to make the comparisons. The data given in Table II also bear directly upon Limitation 2. They represent the average of the results obtained on nineteen stocks which differed from one another only in the percentage and kind of softener, all other conditions being fixed.

The base stock was a high-grade black tread. The data are from the average of three cures on each stock, a correct, slight under, and slight over-cure.

**Table II**

| 16 Hours Bomb | 6 Days Oven | 6 Months Natural | 9 Months Natural | 16 Hours Bomb Equals *Months* | 6 Days Oven Equals *Months* |
|---|---|---|---|---|---|
| Per cent of original tensile product | | | | | |
| 80 | 78 | 83 | 77 | 7.0 | 8.0 |
| Per cent of original modulus at 300 per cent | | | | | |
| 118 | 137 | 137 | 140 | 2.8 | 6.0 |

It is seen that the bomb test in particular shows a quite wide spread, 16 hours being equivalent to 7 or 3 months' natural aging, depending upon whether we take tensile product or modulus as the basis of comparison.

LIMITATION 3—All types of stock, whether using different pigments, different degrees of pigment loading, or different kinds of accelerators, should change in the same manner and degree as in natural aging.

No new data are presented on this point as Tables I and II are sufficient to bring out the fact that the litharge tube stock reacts very differently from the black tread stocks. Furthermore, papers by Park (*1*) and Vogt (*2*) supply additional data.

It seems to the writer that the fact that different accelerators, for example, give widely varying results when compared with natural aging results is one of the most serious criticisms of present methods of artificial aging. If one interprets the results of the unknown on the basis of experience built up on the known and then finds later by sad experience that the new did not behave like the old a very healthy distrust is liable to be engendered in the mind of the experimenter.

### Value of Oxygen Bomb Test

Now in spite of the limitations of present methods the writer believes that artificial aging tests have been of great value to the rubber industry and that in general better aging rubber products are being made now than ever before. In this connection the writer considers the high-pressure oxygen bomb test as proposed by Bierer and Davis to be a sensitive and reliable method for determining the oxidizability of rubber stocks.

In a series of tests involving the determination of the antioxidant properties of approximately three hundred compounds, it has been found that, without exception, those compounds could be classified as good, fair, or worthless by either a high-pressure oxygen test or by the results of natural aging. The method of compounding, previously mentioned in various papers from the Goodyear laboratories, involves the use of acetone-extracted rubber together with zinc oxide, stearic acid, sulfur, and an accelerator with no antioxidant properties such as hexa or D.P.G., to which basic mix is added the compound to be tested for antioxidant properties.

Properly cured sheets of the basic mix will suffer practically complete deterioration in tensile properties in 6 to 12 months in the dark and in even less time in diffuse daylight. A few hours (3 to 5) in the high-pressure oxygen bomb at 70° C. will also accomplish complete loss of tensile properties. Furthermore, the deterioration can be checked equally well by either loss in tensile or decrease in tear resistance.

If one uses the criterion of weight increase as the basis of comparison, the results of artificial and natural aging tests show good correlation, but the lack of complete correlation is probably due to the difficulties of the experimental method (volatility of ingredients, changes due to humidity variations, etc.) rather than to any real significant differences in behavior.

Table III gives the results of variations in tensile product and tear resistance for several widely different stocks which were subjected to a slow oxidation test, the conditions being 150 pounds per square inch (10.5 kg. per sq. cm.) of oxygen at 40° C.

**Table III**

(Per cent of original properties)

| Stock | 7 Days | | 14 Days | | 28 Days | |
|---|---|---|---|---|---|---|
| | T. P. | Tear | T. P. | Tear | T. P. | Tear |
| 1 | 102 | 100 | 110 | 91 | 104 | 95 |
| 2 | 90 | 100 | 75 | 81 | 65 | 75 |
| 3 | 105 | 100 | 110 | 100 | 106 | 95 |
| 4 | 85 | 85 | 72 | 63 | 54 | 61 |
| 5 | 86 | 100 | 85 | 91 | 90 | 80 |
| 6 | 79 | 77 | 58 | 65 | 38 | 48 |
| Average | 90 | 93 | 85 | 83 | 76 | 76 |

On the whole the agreement between the two properties is good. These data are typical and lead to the conclusion that, under test conditions wherein the oxidation effect is enhanced and the heat effect suppressed, both tensile properties and tear resistance are effected in a similar manner.

For those rubber stocks whose life is limited by their oxidizability some form of the high-pressure oxygen test furnishes a reliable qualitative estimate of their worth, but for those stocks whose service is limited by other factors this test is not satisfactory.

In dealing with stocks that are relatively resistant to oxidation, through the use of age-resisting accelerators, proper cure, or antioxidants, the primary effect of the accelerated test is brought about through the elevated temperature employed—i. e., through the heat effect. And in connection with the study of the heat effect widely different results are obtained depending on the criterion used for judging the effect of the heat treatment. For example, a simple rubber 100–sulfur 6.5 stock gives the following tests when heated in nitrogen and air at 70° C.

**Table IV**

(Per cent of original properties)

| | 6 Days | | 12 Days | |
|---|---|---|---|---|
| | Air | Nitrogen | Air | Nitrogen |
| Tensile | 112 | 110 | 84 | 108 |
| Tear resistance | 57 | 63 | 48 | 45 |

The results in Table IV show that the tear resistance suffers much more than tensile properties and that there is little difference between heating in air or nitrogen.

### Importance of Specific Tests

In view of the data presented and of other experiences, it is probably asking too much of any single test to demand that it reproduce quantitatively all of the phenomena associated with natural aging in the same degree on all physical properties, and it is far better to determine by independent tests designed to accentuate one phase and suppress the others the propensities of a stock with regard to oxidizability and after vulcanization.

In the Goodyear laboratories a rather slow oxidation test has been adopted which consists in heating the sheets of rubber in oxygen at a pressure of 150 pounds per square inch (10.5 kg. per sq. cm.) at 50° C. for 6 to 12 days. If they come out of the bomb with fair tensile properties it is fairly certain that the stock is not going to fail by oxidation.

To determine after-vulcanization or stiffening or autopolymerization, or whatever one wishes to call it, the rubber sheets are heated for 6 and 12 days in nitrogen at atmospheric pressure and at a temperature of 70° C. From this test one can judge whether or not a stock is going to become unduly short and brittle on natural aging.

## Literature Cited

(1) Park, *Rubber Age (London)*, **7**, 64 (1926).
(2) Vogt, IND. ENG. CHEM., **17**, 870 (1925).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1017. November, 1929.]

# Correlation of Various Aging Tests with Natural Shelf Aging

**Sidney M. Cadwell**

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ACCELERATED aging tests are employed to predict the probable life of rubber goods—that is, how long it will be before they perish under normal storage conditions. Two accelerated aging tests are widely used. In the Geer aging test (*3*) a sample of the rubber is hung in air at 71° C. (160° F.); 70° C. (158° F.) is the temperature now generally used. Bierer and Davis (*1*) maintain the rubber in oxygen at 60° C. (140° F.) under a pressure of 21.1 kg. per sq. cm. (300 lbs. per sq. in.).

In commercial tests the temperature throughout the aging oven or bomb is not always uniform, and the humidity is rarely maintained constant, although it is known to affect the rate of deterioration (*1*, *4*). Also, conditions of storage vary; light and heat accelerate deterioration or perishing, while high humidity is said to retard it (*6*). These variable factors affect different stocks differently. It is therefore evident that one would hardly expect a given number of hours in the accelerated tests always to equal a given number of months in storage on the shelf.

According to the literature the correlation between the aging tests and natural aging or perishing is only qualitative. Geer and Evans (*3*) showed that one day of aging at 71° C. (160° F.) is roughly equal to 6 months of shelf aging. Tener, Smith, and Holt (*7*) plotted results that show that one day at 70° C. (158° F.) is equal on the average to 5 months of shelf aging, but individual results show that 1 day equals from 2 to 15 months. Reed's results (*5*) show that 1 day at 70° C. (158° F.) is equivalent to less than 6 months.

Bierer and Davis (*2*) found that 10 hours' aging under an oxygen pressure of 21.1 kg. per sq. cm. (300 lbs. per sq. in.) and at 60° C. (140° F.) is equivalent to 1 year of shelf aging for the particular stocks used.

The writer's data show that the oxygen aging and Geer aging tests are in general qualitatively reliable. The stocks which age well in either of these tests usually age well on the shelf. This is particularly true of stocks containing an antioxidant. Such stocks have shown very good aging according to either of the accelerated aging tests, and have also aged very well on the shelf.

It seems desirable to emphasize two specific exceptions to the general statements given above. First, these data show no simple relationship between cracking under tension in the sun and the Bierer oxygen-aging test or the Geer heat-aging test. Second, the bad shelf aging caused by the presence

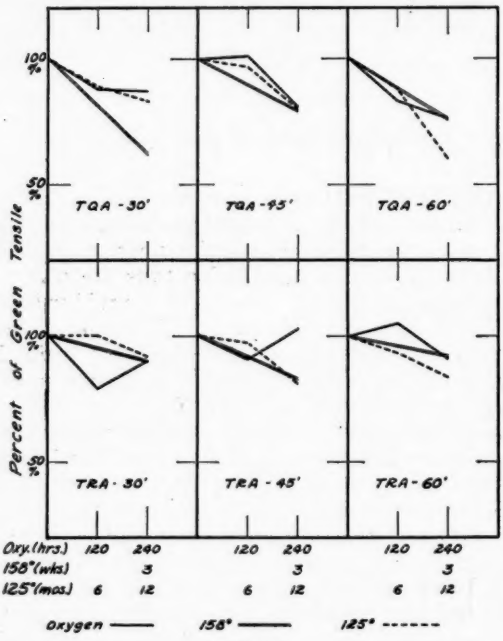


**Figure 1**

of copper or manganese is not adequately predicted by the Geer heat-aging test. The oxygen-aging test is much superior for these stocks because it does forecast the bad aging.

### Experimental Data

In the curves the percentage of deterioration is plotted as the ordinate and the time of aging as the abscissa. In Figure 1 the designation "TQA—30'" refers to a particular stock, TQA, which was mold-cured for 30 minutes in a steam press at 140° C. (40 pounds steam pressure). The 30-, 45-, and 60-minute stocks, therefore, represent different degrees of vulcanization. In the first six curves it is assumed that 240 hours in the oxygen bomb at 60° C. (140° F.) under

21.1 kg. per sq. cm. (300 lbs. per sq. in.) equals 3 weeks at 70° C. (158° F.) and 12 months at 52° C. (125° F.). Aging at 52° C. (125° F.) is taken as standardized and somewhat accelerated shelf aging in storage. 52° C. (125° F.) is so near the temperature of hot storerooms in the summer that a good deal of confidence is placed in results obtained at that temperature.

In Figure 2 the same equivalent times of aging have been employed, and it will be noted again that the curves diverge quite widely, indicating that the correlation is only qualitative. The TSA stock contained antioxidant, while the TTA stock contained no antioxidant. As would be expected, the

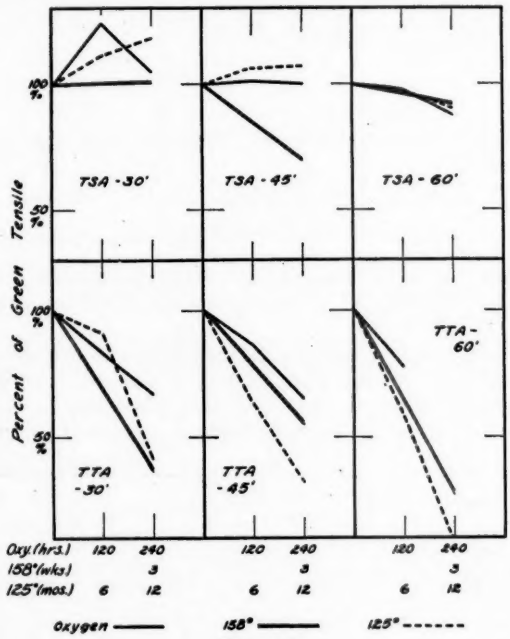


**Figure 2**

stock containing an antioxidant ages very much better. This has been confirmed by actual shelf aging and aging without tension on the roof in the sun.

Figure 3 shows a No. 1 inner tube without antioxidant, and a No. 2 inner tube which contained antioxidant. Here again it will be observed that the correlation is only qualitative.

The curves shown thus far have been with stocks containing zinc oxide and about 3 parts of sulfur per 100 parts of rubber.

Figure 4 shows the comparison of shelf aging under dark storage conditions with aging at 70° C. (158° F.) of the standard vulcanized stock made up of 100 parts of rubber and 10 parts of sulfur. It has been assumed that 1 day at

70° C. (158° F.) is equivalent to 6 months on the shelf. Geer's results indicated that 1 day at 71° C. was equivalent to 6 months of shelf aging. It will be noted that the Geer aging at 70° C. (158° F.) is more severe for the stock that was incompletely vulcanized or undercured—namely, the 180-minute cure—whereas the reverse is true for the somewhat overvulcanized stock which was vulcanized for 240

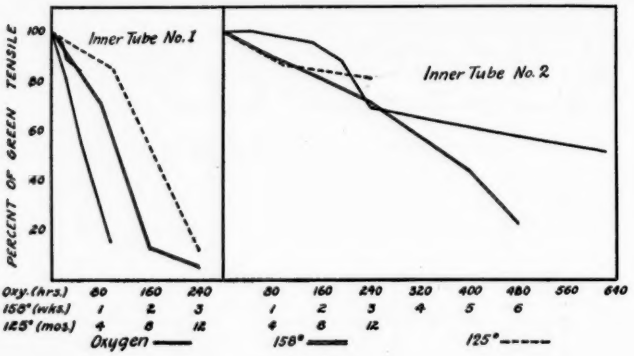


**Figure 3**

minutes. In other words, a correlation which might be very good for one state of vulcanization would not be good for another.

Since amount of sulfur combined with the rubber—i. e., the extent of vulcanization of such a stock—is one of the important variables in the aging, it is interesting to consider a curve showing the relation between combined sulfur and

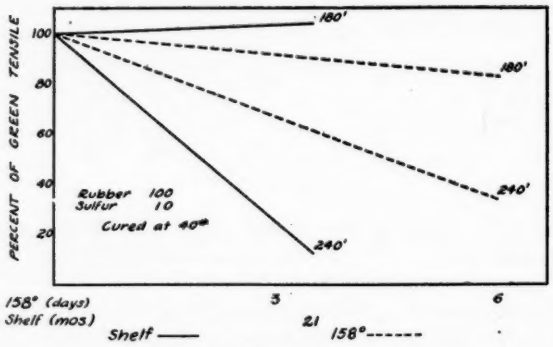


**Figure 4**

hours required for complete deterioration in the oxygen bomb. In this test the greater the number of hours required to deteriorate the stock the better it ages. It will be noted in this curve (Figure 5) that the triangular points fall somewhere near the curve, which indicates that the greater the combined sulfur the poorer the aging. All of these tri-

angular spots represent results with a stock consisting of 100 parts of rubber and 6.6 parts of sulfur with equal amounts of various commercial antioxidants, and it will be noted that the effect of the amount of combined sulfur overshadowed the difference between the antioxidants. The cross represents the time required for the complete deterioration and

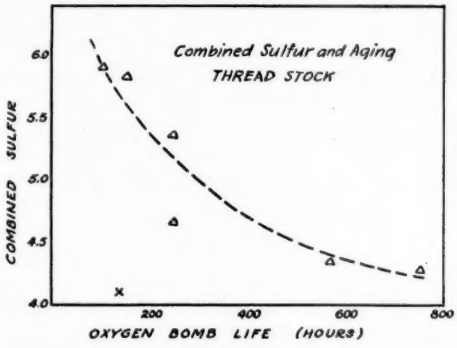


**Figure 5**

the amount of combined sulfur for the blank stock containing no antioxidant. The absence of antioxidant accounts for the rapid deterioration even though the combined sulfur is relatively low. If the stock had contained an antioxidant, the deterioration would have been much slower and the cross would have appeared much further to the right. This

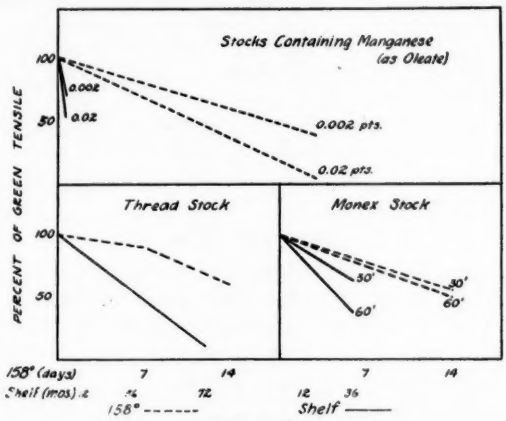


**Figure 6**

demonstrates the well-known fact that antioxidants greatly retard the deterioration when other factors, such as the amount of combined sulfur, are taken into consideration.

In Figure 6 the lower left-hand curve shows the results of shelf and 70° C. (158° F.) aging with a thread stock. The thread stock consists of 100 parts of rubber and 6.6

parts of sulfur, and it will be observed that the correlation is only qualitative on the assumption that 1 day at 70° C. (158° F.) equals 6 months on the shelf. The same is true of the lower right-hand curve, in which a stock consisting of 100 parts of rubber, 10 parts of zinc oxide, 3 parts of sulfur, and 0.1 part of the accelerator Monex was employed. In this case almost the same results were obtained with a similar stock containing the accelerator Tuads. In the top set are shown results obtained with stocks containing the indicated amounts of manganese. It will be noted that according to the 70° C. (158° F.) test these stocks aged quite well, but in actual shelf aging they deteriorated very rapidly indeed. Very similar results were obtained with copper. This shows that the 70° C. (158° F.) Geer test does not adequately predict the bad aging of stocks containing copper or manganese. After oxygen-aging these same stocks for 120 hours they were so badly deteriorated that they could not be tensiled at all. In other words, the oxygen-aging test did predict the bad shelf aging. To the writer this is quite important because manganese and copper occur as impurities in many fillers and sometimes even in cotton and rubber; therefore, they are a fruitful cause of unexpected deterioration.

## Conclusion

In view of the many variables involved in accelerated and shelf aging, and of the fact that the correlation between the two is only qualitative, it is believed that there are two practical answers to the aging problem. One is incessant care. If the stock is properly balanced, if certain impurities are absent, and if the state of vulcanization is correct, good aging will be obtained. The other answer, which seems to be safer, is to use antioxidants. A certain antioxidant has always improved the aging of all sorts of stocks under all conditions; probably other antioxidants will do as well. Therefore, the use of antioxidants is the practical answer to the aging problem.

## Acknowledgment

The author desires to express his indebtedness to J. W. Temple and M. W. Mead for their valuable assistance in the preparation of this paper, and to J. F. Reid for a portion of the data.

## Literature Cited

(1) Bierer and Davis, IND. ENG. CHEM., **16**, 711 (1924).
(2) Bierer and Davis, *Ibid.*, **17**, 860 (1925).
(3) Geer and Evans, *India Rubber World*, **64**, 887 (1921).
(4) McKee and Depew, IND. ENG. CHEM., **20**, 484 (1928).
(5) Reed, *Ibid.*, **21**, 316 (1929).
(6) Stevens, *India Rubber J.*, **61**, 310 (1921).
(7) Tener, Smith, and Holt, Bur. Standards, *Tech. Paper* **342** (1927).

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 11, page 1019. November, 1929.]

# Correlation between Geer Oven and Natural Aging of Selected Tire Compounds

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THE Geer oven used was the standard equipment with circulating air, and tests were made at 70° C. The samples for the natural or shelf-aging tests were placed one upon the other on shelves at ordinary room temperature which varied from 65° to 90° F. (18° to 32° C.) depending on the season.

An attempt was made to correlate these Geer tests with shelf-aging tests in a broad way, but all generalizations which suggested themselves were open to serious objections. For instance, the shelf-aged results showed that certain carcass and tread compounds accelerated with an aldehyde-amine type of accelerator aged considerably better than similar compounds accelerated with a guanidine. These same compounds when aged in the Geer oven do not show the same relative deterioration. Since this difference is due solely to the accelerator used, it is evident that an accurate comparison between oven- and shelf-aged tests can be made only when the same accelerator is used throughout the test. The writers therefore selected stocks accelerated with phenyl-*o*-tolylguanidine, which had been oven-aged 4, 8, and 12 days, and shelf-aged 1, 2, and 3 years, and confined themselves to two standard tread compounds and three standard carcass compounds as follows: (*a*) all-rubber tread compound (sp. gr. 1.30), (*b*) 10 per cent shoddy tread compound (sp. gr. 1.13), (*c*) pure-gum carcass compound, (*d*) 5 per cent shoddy carcass compound, and (*e*) 30 per cent shoddy carcass compound.

The modulus at 300 per cent for tread compounds, the modulus at 500 per cent for carcass compounds, also the elongation, tensile strength, and tensile product were tabulated for each compound and cure. To give quantitative expression to the test data, each result was calculated as a percentage of the original result for each of the four criteria.

For example, if the modulus at 300 per cent on a tread stock was 1000 pounds per square inch (70.5 kg. per sq. cm.) for 25-minute cure at 290° F. (143° C.) on the 1-year natural test and the modulus for the original test was 850 pounds per square inch (59.9 kg. per sq. cm.), the result would be expressed in percentage of the original, or 117.8 per cent. These percentages were then averaged and these averages are given in the accompanying table. On (*a*) and (*b*) twenty tests were used for the 1- and 2-year tests, and also for the 4- and 8-day tests, while ten tests were used for the 3-year and 12-day tests. For the carcass stocks, (*c*), (*d*), and (*e*), twenty-two results were used for the 1- and 2-year and 4- and 8-day tests. For the 3-year and 12-day tests six tests were compared. The ratio percentages below each figure were obtained by dividing the oven percentages by the natural percentages.

The range of cures at 290° F. (143° C.) was 25 to 100 minutes for the tread compounds and 15 to 35 minutes for the carcass compounds. These included under cures, optimum, and over cures on all compounds.

**Comparison of Natural and Oven Aging of Tread and Carcass Compounds**

(Calculated as percentage of original result)

| Kind of Aging | Modulus | | Elongation | | Tensile Strength | | Tensile Product | |
|---|---|---|---|---|---|---|---|---|
| | Tread | Carcass | Tread | Carcass | Tread | Carcass | Tread | Carcass |
| | % | % | % | % | % | % | % | % |
| Natural, 1 year | 120.6 | 144.9 | 90.7 | 93.6 | 82.6 | 101.5 | 74.2 | 91.1 |
| Oven, 4 days | 131.4 | 122.8 | 88.1 | 99.4 | 81.5 | 96.4 | 72.2 | 92.1 |
| Ratio | 108.9 | 84.7 | 97.1 | 106.2 | 98.6 | 95.0 | 97.3 | 101.1 |
| Natural, 2 years | 157.9 | 148.5 | 71.7 | 87.6 | 65.5 | 77.4 | 46.5 | 68.8 |
| Oven, 8 days | 124.0 | 111.9 | 78.3 | 92.5 | 59.7 | 80.4 | 47.6 | 74.6 |
| Ratio | 78.5 | 75.3 | 109.2 | 105.6 | 91.1 | 104.0 | 102.3 | 108.4 |
| Natural, 3 years | 139.5 | 109.4 | 66.8 | 89.6 | 45.2 | 56.8 | 30.8 | 51.8 |
| Oven, 12 days | 119.7 | 92.0 | 63.2 | 82.5 | 39.3 | 36.1 | 25.8 | 29.5 |
| Ratio | 85.8 | 84.1 | 94.6 | 92.0 | 86.9 | 63.5 | 83.7 | 56.9 |

Modulus—It will be seen that under shelf-aging conditions for carcass and tread compounds the modulus stiffens in 1- and 2-year tests and then softens in the third year. In the oven aging the modulus stiffens in 4 days and softens in 8 and 12 days. The effect of the heat of the oven is quite marked.

Elongation—The 1-, 2-, and 3-year natural-aged tests show successive increases in stiffness as evidenced by the decreasing elongation. The oven results also show this stiffening but to a lesser extent. The agreement of the oven and natural results is considerably better than in the case of modulus.

Tensile Strength—In the case of the tread compounds the 1-, 2-, and 3-year natural as well as the 4-, 8-, and 12-day oven tests show successive decreases in tensile strength, and we consider that these results are in fairly close correspond-

ence. Considering the carcass stocks, the 1-year natural tensile is slightly more than original, while the 4-day oven test shows a slight decrease. The 2-year and 8-day oven tests correspond quite closely; however, the 3-year and 12-day tests show a large variance.

TENSILE PRODUCT—In this case the softening effect of the heat of the oven is counterbalanced by the extra decrease in tensile strength. This produces a satisfactory agreement for the tread compounds and also the carcass compounds for 1 and 2 years and 4 and 8 days. As before, the 3-year and 12-day carcass-stock tests check very poorly.

## Summary of Results

In standard guanidine tread and carcass compounds, test results obtained from the 4- and 8-day periods in the Geer oven at 70° C. correspond approximately to 1 and 2 years of natural aging. Data obtained from the 12-day period correspond with 3 years of natural aging for tread compounds, but results showed no relation between these same periods for carcass stocks.

The tensile product is the criterion which shows the best correspondence between Geer oven tests and natural aging tests on the tread and carcass compounds used.